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The Philosophical Magazine

FIRST PUBLISHED IN 1798

A Journal of Theoretical Experimental and Applied Physics

Vol. 5

April 1960
Eighth Series

No. 52

25s. 0d., plus postage

Annual Subscription £13 10s. 0d., payable in advance



Printed and Published by

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Observations on Extensive Air Showers

VIII. The Distribution in Declination and Curvature of the Shower Front†

By E. F. BRADLEY and N. A. PORTER‡
Atomic Energy Research Establishment, Harwell

[Received November 9, 1959]

ABSTRACT

A directional Čerenkov counter has been used at latitude 52° N to separate shower directions into two classes, incident from North and South of the East–West plane through the zenith. Evidence from some previous experiments indicates a Northern excess of approximately 30%. No excess has been observed; out of 526 showers, each containing at least 3×10^6 particles at sea level, 261 were incident from the North, and 265 from the South. The apparent direction of a shower was found to be dependent on the position of its axis relative to the detector. A directional radius of curvature was measured, making reasonable assumptions, and found to be $1625 \pm_{290}^{505}$ metres.

§ 1. INTRODUCTION

A NUMBER of experiments on large air showers have shown marked anisotropies in the distribution of shower directions in declination, though without appreciable effects in right ascension (McCusker 1959). The assignment of declination coordinates to showers may be strongly affected by small systematic errors in measurement, and these errors are not, as in the case of right ascension, eliminated by the rotation of the earth. Nevertheless, the statistical significance of the effects is high, and the distributions observed in different experiments are rather similar, showing an anomalously large number of showers from Northern directions.

An experiment has been carried out with a directional Čerenkov counter on the Culham array, latitude 52° N (Cranshaw and Galbraith 1957 a, b) to divide shower directions into two classes, incident North and South of the East–West zenith plane in laboratory coordinates. If the distribution of shower directions is isotropic, the same number of showers should be observed in the two classes. A distribution similar to that given by the M.I.T. group (Clark *et al.* 1957) for showers containing more than 2×10^6 particles, would give rise to a ratio in numbers $N/S \approx 1.30$.

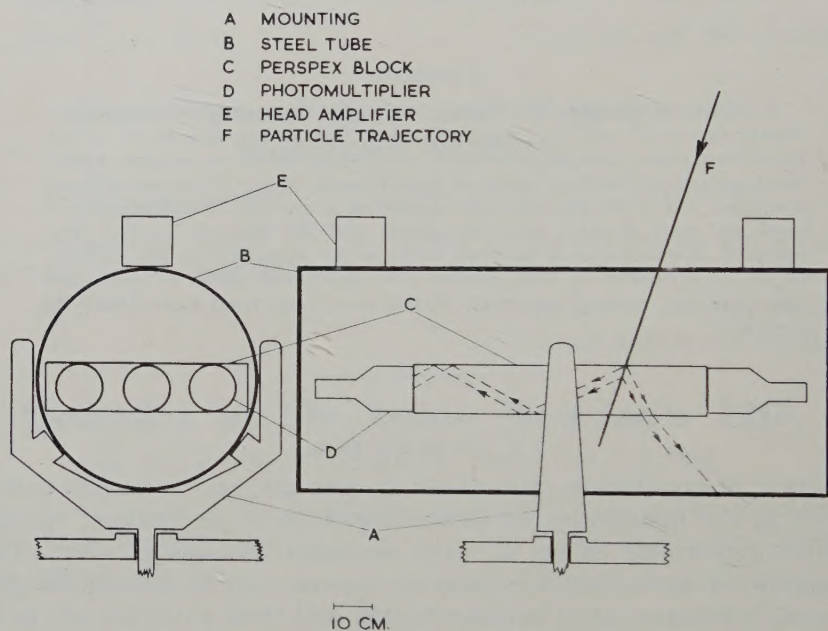
† Communicated by the Authors.

‡ Now at University College, Dublin.

§ 2. EXPERIMENTAL METHOD

The detector was a laminated parallelopiped of Perspex (refractive index 1.49) with dimensions $80 \times 53 \times 12.5 \text{ cm}^3$. It was supported along two lower edges in a horizontal steel tube (fig. 1) so that Čerenkov light produced by charged particles in it was retained only by multiple total internal reflection. Three 5 in. photomultipliers connected in parallel, were mounted in optical contact at each of the end faces. Signals from each of the two sets of photomultipliers were amplified separately and displayed on a recording oscilloscope.

Fig. 1



A particle incident normally on the block gave a signal approximately equal in the two sets of photomultipliers, since all the light was retained, and collected in approximately equal parts at both ends roughly independent of the position. A particle incident obliquely at the upper face of the block, however, gave a signal larger in the photomultipliers towards which it was directed, since some of the Čerenkov light was lost at the lower surface of the block. Showers could therefore be assigned to northerly or southerly directions from the ratio of signals in the two sets. The theory of the detector has been considered in the book by Jelley (1958, pp. 138-141).

In a subsidiary experiment, carried out with a Geiger telescope selecting μ -mesons, the directional response was determined. For showers, averaging over all azimuth and zenith angles, and using the zenith distribution

found by the M.I.T. group, the mean signal in the preferred channel was then calculated to be roughly three times that in the other channel.

Statistical fluctuations in the number of photo-electrons produced, together with variations in mean pulse height over the surface of the block, gave rise to an uncertainty in the assignment of showers into the two classes. The probability, averaged over all zenith and azimuth angles, that a single particle was assigned to the wrong class, was 0.07. If more than one shower particle was observed this probability was considerably less. The contribution from these sources to the total statistical error is roughly 27% of the Poisson error in N/S .

In addition to the uncertainties in measurement of particle directions, the mean direction of the particles observed in any region of the shower will not correspond exactly to the axial direction. Two effects occur: (a) a systematic tendency for particle directions to diverge from the axial direction, increasing with distance of observation from the axis; and (b) the fluctuations of individual particles about the mean direction. The systematic effect was detected experimentally, and has been used to estimate the directional radius of curvature, i.e. the mean height (in the case of a vertical shower) at which particle directions projected from sea-level approach most nearly to the axis. The directional radius of curvature is comparable in magnitude with the radius of the shower front, which has been measured by several workers (Bassi *et al.* 1953, Greisen 1957) and is between 1.5 and 2.5 km. The relation between the two depends on the nature of the cascade process, on which very little reliable information is available. Particles deflected by multiple scattering alone, and reaching sea level without bremsstrahlung or appreciable loss of energy by ionization will project back to a height $2h/3$, where h is the height at which they left the axis (Scott 1949). Physically the process is more complex, since discontinuous losses of energy occur in bremsstrahlung, and in part of the trajectory the energy is carried by γ -rays. It would be expected, however, that the directional radius of curvature would lie between $2h/3$ and h , the radius of the shower front. Monte Carlo calculations are in progress on this problem.

The effects of fluctuations in individual particle directions on the overall N/S ratio is small, if the r.m.s. deviation is taken to be 10° , a value expected from electromagnetic cascade theory, and compatible with cloud chamber observations. In the present case, roughly half the events were single particle observations, and the contribution to statistical errors from fluctuations of this kind will be approximately 25% of the Poisson distribution in N/S .

If a true N/S excess exists, the mean value observed will be reduced somewhat because of these fluctuations. For a true value 1.30, the experimentally expected value is 1.24.

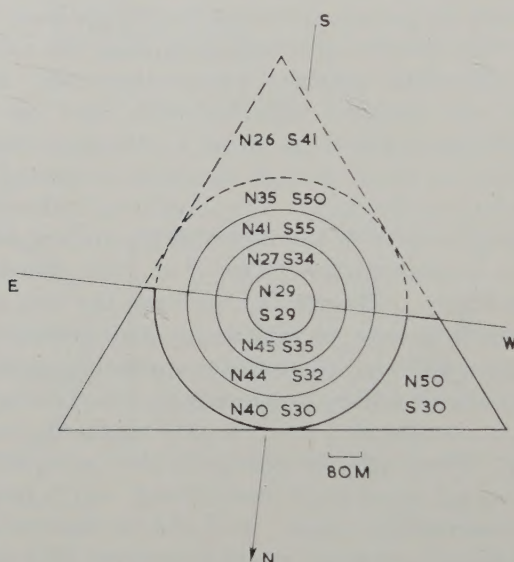
The detector was mounted in a caravan at the centre of the array. It was rotated through 180° , about a vertical axis, every 24 hours, so that the two sets of photomultipliers faced alternately North and South.

§ 3. RESULTS

3.1. *North/South Ratio*

3075 showers have been observed on the array during one run. 673 of these could be assigned in direction, 16 gave signals which saturated both channels of the detector, 17 gave pulses equal in both channels, within the errors of measurement, and 2369 gave no signal in either channel. The distribution of assignable shower directions, in relation to the position of the core on the array, is shown in fig. 2. Taking only showers which fell in the circular area of 320 metres radius, the distribution of shower cores was almost uniform about the East–West line, 255 falling North, and 271 South.

Fig. 2



The direction of showers in this area were: 261 northerly, 265 southerly. These figures may therefore be used to determine the North/South ratio:

$$N/S = 0.99 \pm 0.12.$$

The probability that this result be consistent with a true value $N/S \geq 1.30$, is about 0.01 on a χ^2 -test. Over the whole array, 337 showers were assigned to northerly directions, and 336 to southerly directions. The statistical error includes that due to uncertainties in classification of direction, and to the difference in numbers of showers falling North and South of the East–West line.

3.2. *Radius of Curvature*

It may be seen from fig. 2 that showers falling North of the detector show a northerly directional excess, and showers falling South, a southerly excess. Assuming a zenith angle distribution $dN d\theta = K \cos^{11} \theta d\theta$, which is

similar to that found by Clark *et al.* (1957) and integrating numerically over each half annulus for zenith, azimuth, *direction* and distance from the detector, the directional radius of curvature may be found. Values are shown as a function of distance from the shower axis, in the table:

Directional Radii of Curvature

Distance from axis, metres	Directional radius metres
80-160	1040 + 1490 - 350
160-240	1380 + 830 - 345
240-320	1840 + 1130 - 460
> 320	1925 + 1155 - 565
Weighted mean value 80-320	1625 + 505 - 290

An increase of radius of curvature with increasing distance from the core would be expected, but the measurements are insufficiently accurate to establish it. The differences in total numbers of showers falling in corresponding North and South half-annuli arise from the granular structure of the array, and have no systematic effect on either the North/South ratio or the curvature measurements.

§ 4. DISCUSSION

It is unlikely that a broad anisotropy could be masked in the present experiment by systematic errors. The rotation of the counter serves to eliminate errors due to differences in response of the two channels, or departure of the counter from the horizontal. Residual errors could arise from the following causes:

(a) Departure of the axis of rotation from the vertical. This has been tested, and is less than 0.25° , corresponding to a maximum error of 0.5% in N/S.

(b) Change of gain of the photomultipliers with rotation in the earth's magnetic field. Since both the caravan and counter housing are steel this effect is small, and an upper limit of 2% may be set by the change in response to vertical μ -mesons observed in the two positions.

(c) Asymmetries in the external surroundings of the detector. These are difficult to calculate, but believed to be small. The caravan was aligned along an East-West line, so that the distribution of absorbing material was

symmetric at zenith angles up to 45° . There is no reason to believe that the main array has any preferred direction of selection.

Finally, the observation of directional asymmetries, related to the position of the shower core, lend confidence to the belief that the directional discrimination of the detector is reliable. If Coulomb scattering is assumed to be dominant in causing the lateral spread of the particles, the directional radius of curvature found corresponds to a mean radius of curvature of the shower front of $2440 \pm {}^{760}_{430}$ metres, consistent with the value of 2600 metres found by Bassi *et al.* (1953). This value is larger than that found by Greisen (1957) but since it is reasonable to suppose that the radius of curvature will change with distance from the core, the discrepancy is not serious.

§ 5. CONCLUSIONS

The results are inconsistent with the existence of a broad anisotropy in the declination distribution of showers which has an amplitude comparable with that pointed out by McCusker, but do not exclude the possibility of point sources which make small contributions to the total flux.

ACKNOWLEDGMENTS

The authors would like to thank Professor C. B. A. McCusker for communication of results before publication; Dr. T. E. Cranshaw, Dr. W. Galbraith, and Dr. G. W. Clark for discussion of this paper in manuscript.

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The Relative Abundances of the Heavy Nuclei in the Primary Cosmic Radiation†

By C. J. WADDINGTON

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[Received December 22, 1959]

ABSTRACT

In an attempt to resolve the present controversy about the relative abundances of the heavy, $Z \geq 6$, nuclei in the primary cosmic radiation, the magnitude of the corrections introduced by the overlying atmosphere has been redetermined. For this reason it has been necessary to use nuclear emulsions to determine the fragmentation parameters of nuclei having $20 \leq Z \leq 28$. The results of this work show that the relative abundances calculated previously by considering the diffusion of nuclei through the atmosphere were not seriously in error, and that outside the atmosphere the ratio of H , $Z \geq 10$, to M , $6 \leq Z \leq 9$, nuclei is 0.38 ± 0.04 . The significance of this result is considered briefly.

§ 1. INTRODUCTION

DURING recent years determinations of the chemical abundances of the nuclei in the primary cosmic radiation have been the cause of considerable controversy. In particular, the vexed question of the abundances of those nuclei with $3 \leq Z \leq 5$, the L -nuclei, has been the subject of many experiments, overshadowing, to some extent, the equally important determinations of the abundances of the heavier nuclei. For these heavier nuclei it was generally assumed, without much discussion, that the ratio $R(x)$, at a depth in the atmosphere of x g/cm², of those nuclei with $Z \geq 10$, H -nuclei, to those with $6 \leq Z \leq 9$, M -nuclei, was about 0.4 at the top of the atmosphere, R_0 . However, in a recent experiment, Appa Rao *et al.* (1958) have presented evidence that the true value of R_0 may well be less than 0.3, and indeed their results can be interpreted as predicting $R_0 \leq 0.2$.

These authors consider that in previous experiments the corrections that have had to be made for the effects of the residual atmosphere above the points of detection have been seriously miscalculated. In particular, they remark that since nuclei with mass numbers as high as 56 to 58 do occur in the primary radiation, the H group includes nuclei covering a wide range of masses. Thus it is not permissible to assume that the behaviour of this group can be represented by a constant mean free path for interaction, nor that the mean mass of the nuclei in the group will not change rapidly as they traverse matter. Both these assumptions had been implicit in the calculations made in earlier papers. Instead, these authors measured directly the variation of $R(x)$ with x , the depth in the

† Communicated by the Author.

atmosphere, and thus obtained a growth curve, which, when extrapolated to the top of the atmosphere, suggested that $R_0 \leq 0.2$. By considering the ratio $H/(H+M)$ instead of R , these authors obtained a value for R_0 of 0.29, but the superiority of this result over that obtained by considering R is not at all clear.

Because of the discrepancy between these results and those obtained previously, it was felt that it would be valuable to refine the earlier calculations on the effects of the overlying atmosphere, in order to see whether this divergence could be resolved. Such a refinement can be achieved by separating the H -nuclei into two groups, so that the assumptions of constant mean free path and mean charge or mass are more closely satisfied. In making these corrections it is usual to consider that a diffusion of the nuclei occurs as they pass through the atmosphere, Kaplon *et al.* (1954), and it is necessary to know the interaction mean free paths of each component, together with the number of fragments belonging to the lighter components produced in typical interactions, the fragmentation parameters. It was thus necessary to determine these quantities for the two groups of nuclei being considered, those with $10 \leq Z \leq 19$, $\mathcal{H}$ -nuclei, and those with $20 \leq Z \leq 28$, $\mathcal{V}\mathcal{H}$ -nuclei. Values for these quantities have been derived and are presented in this paper, together with the results obtained by using them to correct previous experimental data for the effects of the overlying atmosphere.

§ 2. EXPERIMENTAL DETAILS

Three stacks of nuclear emulsions were used. Of these, two, the G and I stacks, were exposed over Northern Italy at an altitude of about 100 000 feet, while the third, the T stack, was exposed over Texas, U.S.A., at about 125 000 feet. Details of the physical dimensions and exposure characteristics of these stacks are given in table 1. Since the geomagnetic cut-off energy for vertical incidence over Northern Italy and Texas are, in both cases, about 1.5 BeV per nucleon, Fowler and Waddington (1957) and Freier *et al.* (1959), only a few of the nuclei recorded were non-relativistic.

The top edges and sides of the emulsions were scanned for the tracks of nuclei which satisfied the following conditions:

- (i) The tracks should have a projected length of at least 1 mm in a 600 micron emulsion.
- (ii) The tracks should not make an angle with the vertical of more than 60° .
- (iii) The tracks should be at least as heavy as those produced by silicon nuclei, $Z = 14$.

Due to the relative thinness of the T stack, which only consisted of 70 emulsions, condition (i) was modified for those tracks found on the top edges of this stack; the minimum length required being set at 2 mm per emulsion.

The charges of the nuclei were roughly measured by counting on each track 100 δ -rays which extended more than 2.7 microns from the core of the track. These measurements, while naturally insufficient to give resolution between individual charges did, in each stack, show a separation between a group of the heaviest nuclei and those of lower charge. Due to the apparent low relative abundance of those elements having $15 \leq Z \leq 19$, in the cosmic radiation, see e.g. Waddington (1960), this heavy group has been assumed to be due to $\mathcal{V}\mathcal{H}$ -nuclei, and the others to $\mathcal{H}$ -nuclei. Confidence in this interpretation was increased by the observation of several interactions of the type where α -particles were the only products other than the residual nucleus. In each case there was a measurable decrease in the apparent charge, of an amount consistent with the assumption that this group of heavy nuclei did not have a range of charges much greater than six.

Table 1. Physical Dimensions and Flight Characteristics of Emulsion Stacks

	Volume				Date of exposure	Duration of exposure (hours)	Altitude (feet)	Location
	cm	cm	cm	No.				
G	27	$\times 37$	$\times 0.06$	250	12.10.54	6.0	85 000	N. Italy
I	25	$\times 38$	$\times 0.06$	60	20. 9.55	6.67	100 000	N. Italy
T	20	$\times 15$	$\times 0.06$	70	8. 2.59	15.2	125 000	Texas

Some of these apparent $\mathcal{V}\mathcal{H}$ -nuclei were actually nuclei of lower charge which had lost sufficient energy by ionization for their tracks to appear as heavy as those of relativistic $\mathcal{V}\mathcal{H}$ -nuclei. A number of these could be eliminated because they were brought to rest before going 10 cm, the approximate range of a 1 BeV per nucleon $\mathcal{V}\mathcal{H}$ -nucleus, others because in their interactions they produced α -particles, whose grain density showed that they were of low energy. Of the 278 nuclei which were assumed, from the original δ -ray count, to be $\mathcal{V}\mathcal{H}$ -nuclei, 165 provided an indication of the velocity. About 22% of these were non-relativistic, and just over 4% appeared to be actually $\mathcal{H}$ -nuclei. Thus probably less than 5 of the 113 nuclei whose velocities were unknown could have been $\mathcal{H}$ -nuclei.

The 184 interactions observed as a result of tracing the tracks of the $\mathcal{V}\mathcal{H}$ -nuclei through the emulsions from the point of location in the stack were analysed if they satisfied the following conditions.

- (i) Provided the potential range in the stack after the point of interaction was greater than 2.0 cm the interaction was fully analysed. This condition was necessary in order to provide sufficient range for the definite identification of any α -particles emerging from the interaction.

- (ii) If the potential range was between 20 and 5 mm, then only those fragments of the incident nucleus with $Z \geq 3$ were considered.
- (iii) Interactions within 5 mm of the exit point from the stack were not analysed.

Each interaction was classified in terms of the number of black and grey tracks produced by particles emitted from the target nucleus, N_h ; the number and type of fragments having $Z \geq 3$ emitted by the incident nucleus, n_Δ ; the number of α -particles from the incident nucleus, n_α ; and the number of tracks producing less than 1.4 times the minimum ionization, n_s . Due to the rather low minimum in some of these emulsions, and the complexity of some of the interactions, these values of n_s cannot be regarded as very reliable, and no estimates of the meson multiplicity are possible from these data. In every case where $n_\alpha \geq 1$, 500 grains were counted on at least one α -particle in order to have a measure of the velocity of the primary nucleus. The analysed interactions are listed in table 2.

The charges of the secondary nuclei were determined either by counting 100 δ -rays of more than four grains on the tracks of nuclei with $Z \leq 10$, or by counting 100 δ -rays which projected more than 2.7 microns from the track. Normalizing these measurements against those made previously in the I and G stacks, see Rajopadhye and Waddington (1958), and using charge indicating interactions in the T-stack, it was possible to determine Z in the range 3–10 to within plus or minus half a charge, and above 10 to assign the nuclei to a charge group.

§ 3. RESULTS

3.1. *Mean Free Path*

After suitable corrections had been made to the observed path lengths to eliminate systematic biases, 174 nuclear interactions were observed in a total path length of 1519.6 cm. The resulting mean free path is 8.72 cm, or 33.3 ± 2.5 g/cm² in nuclear emulsion having a density of 3.82 g/cm³. This value may be compared with those of 29.4 g/cm² for $\mathcal{V}\mathcal{H}$ -nuclei having a mean mass number $\bar{A} = 54$, and 39.2 g/cm² for $\mathcal{H}$ -nuclei having $\bar{A} = 27$, which are calculated from the semi-empirical relation proposed by Bradt and Peters (1950) for the cross section, σ , of

$$\sigma = \pi(1.45 \times 10^{-13})^2(A_1^{1/3} + A_2^{1/3} - 2\Delta R)^2. \quad . \quad . \quad (1)$$

Thus the mean free path obtained experimentally appears to be significantly different from that predicted for $\mathcal{V}\mathcal{H}$ -nuclei, corresponding to $\bar{A} = 40 \pm 7$. This discrepancy, if real, could be due to: (a) failure of eqn. (1) to give the true mean free path for these heavy nuclei; (b) a failure to detect some of the nuclear interactions produced; (c) the inclusion of a number of $\mathcal{H}$ -nuclei in the sample considered. Of these possibilities (b) appears to be the most likely since; (a) eqn. (1) has been experimentally confirmed over a range of incident and target nuclei which extends from α -particles passing through air to H -nuclei passing through lead, see e.g.

Table 2. Interactions marked with * are those which occurred between 20 and 5 mm of an Exit Point

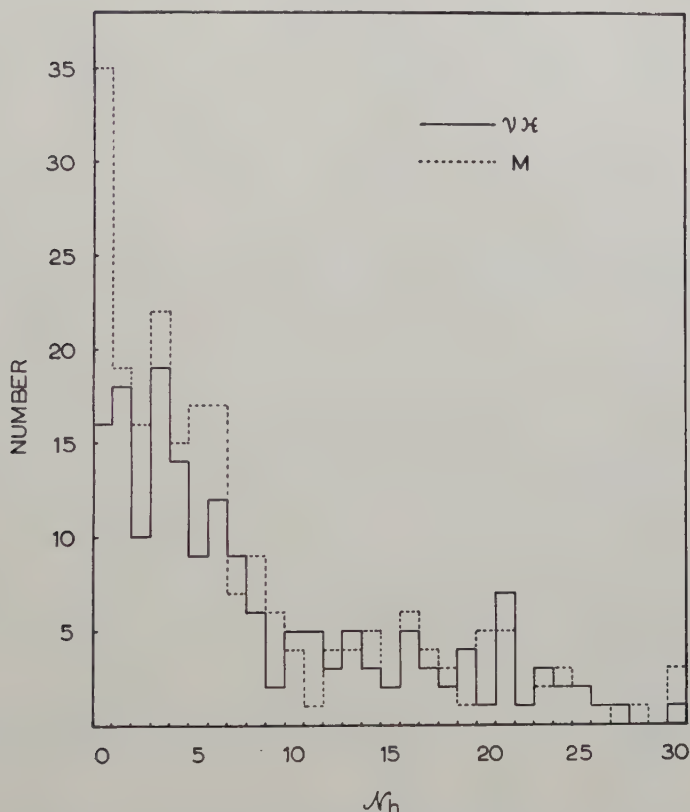
N_h	n_Δ	n_α	n_s	N_h	n_Δ	n_α	n_s
0	$\mathcal{H} + \text{Be}$	0	4	2	Li	1	21
0	$\mathcal{H} + \text{Li}$	1	?	3	$\mathcal{V}\mathcal{H}$		5
0	$\mathcal{H}$	3	11	3	$\mathcal{V}\mathcal{H}$		2
0	$\mathcal{H}$	3	5	3*	$\mathcal{V}\mathcal{H}$		2
0	$\mathcal{H}$	3	4	3	$\mathcal{V}\mathcal{H}$		2
0	$\mathcal{H}$	2	2	3	$\mathcal{V}\mathcal{H}$		1
0	$\mathcal{H}$	1	7	3	$\mathcal{V}\mathcal{H}$		0
0	$\mathcal{H}$	1	4	3*	$\mathcal{V}\mathcal{H}$		0
0	$\mathcal{H}$	1	0	3	$\mathcal{H}$	3	10
0	C+N	2	5	3	$\mathcal{H}$	3	6
0	Be+Li	0	52	3	$\mathcal{H}$	1	7
0	C	4	7	3	$\mathcal{H}$		19
0	C	1	14	3	$\mathcal{H}$		13
0		2	25	3	$\mathcal{H}$		10
0		2	24	3	Be+Be	1	16
0			?	3*	Li	7	7
1	$\mathcal{V}\mathcal{H}$		2 p	3	Li	4	18
1*	$\mathcal{V}\mathcal{H}$		1 p	3*		4	14
1	$\mathcal{H} + \text{Li}$	1	17 not p	3		3	22
1	$\mathcal{H}$	4	6 p	3			15
1	$\mathcal{H}$	3	3 p	4	$\mathcal{V}\mathcal{H}$		3
1	$\mathcal{H}$	2	0 p	4	$\mathcal{H}$	2	9
1	$\mathcal{H}$		3 not p	4*	$\mathcal{H}$	2	7
1	$\mathcal{H}$		1 p	4	$\mathcal{H}$	2	4
1	C+Li	4	16 p	4	$\mathcal{H}$	1	7
1	F	2	8 p	4	$\mathcal{H}$		9
1	O	1	16 not p	4	$\mathcal{H}$		8
1	Li	5	8 not p	4	C	5	13
1	Li	3	13 not p	4	B	4	20
1		3	17 p	4	B	1	25
1		1	29 p	4	Be	3	13
1		1	24 p	4		6	18
1			25 p	4		5	17
?	$\mathcal{H}$		4	4		2	22
2*	$\mathcal{V}\mathcal{H}$		4	5	$\mathcal{V}\mathcal{H}$		2
2	$\mathcal{V}\mathcal{H}$		0	5	$\mathcal{H}$	3	3
2	$\mathcal{H}$	2	8	5	$\mathcal{H}$	2	4
2	$\mathcal{H}$	2	2	5	$\mathcal{H}$	1	16
2	$\mathcal{H}$	1	15	5	$\mathcal{H}$	1	9
2	$\mathcal{H}$	1	10	5*	C+N+Li		10
2	$\mathcal{H}$	1	4	5	B+Li	2	12
2	$\mathcal{H}$	1	3	5	C	4	12
2	Li	3	17	5	Li	4	17

Table 2 (continued)

N_h	n_Δ	n_α	n_s	N_h	n_Δ	n_α	n_s
6	VH		4	13	Be + Be	1	12
6*	VH		4	13		4	20
6	VH		2	13*			60
6	VH		0	14	H	2	8
6	H	2	7	14*	Li	4	7
6	H		7	14		1	24
6	H		4	15		1	45
6*	F	2	14	15			?
6	O	2	6	16	H	2	10
6*	B + Li	2	9	16	O	2	12
6		4	33	16		3	51
6			53	16*			100
7	H	3	7	16			28
7	H	3	4	17	Be	3	20
7*	H	2	7	17		2	31
7	H	1	8	17		2	20
7	H	1	4	18	H	2	6
7	N	3	10	18		4	34
7	C	2	13	19	Li		38
7	Be	3	18	19		2	30
7		1	39	19		2	25
8	VH		4	19		1	42
8	H		2	20			39
8	H		2	21*		7	9
8	C	2	11	21*		4	25
8		4	12	21*		2	19
8			100	21		2	?
9	H	1	11	21			27
9*	H		6	21			25
10	H	1	15	21			25
10	C	3	10	22		1	21
10	B	4	9	23	B	1	16
10		3	44	23			45
10			100	23			24
11	VH		4	24		1	32
11*	VH		1	24			34
11	H		7	25	B	1	42
11		4	22	25		2	23
11			120	26		3	10
12	H	1	7	27		2	29
12	O	1	10	30	N		16
12		4	43	31			35
13*	H	2	13	32		4	14
13	H	2	7	37		1	23

Rajopadhye and Waddington (1958); (c) the selection of $\mathcal{V}\mathcal{H}$ -nuclei appears stringent enough to eliminate most, if not all, of the $\mathcal{H}$ -nuclei, whereas the observed mean free path suggests a contamination of over 60% with nuclei having $\bar{A} = 32$. Such an effect is in contradiction to our present ideas regarding the relative abundances of $\mathcal{V}\mathcal{H}$ -nuclei and nuclei with $15 \leq Z \leq 19$. On the other hand, it is quite plausible that interactions should be missed while following along the tracks of $\mathcal{V}\mathcal{H}$ -nuclei.

Fig. 1



Comparison of the N_h distributions of interactions in emulsion produced by $\mathcal{V}\mathcal{H}$ and M -nuclei.

Those interactions which are most likely to be missed by an observer tracing along the track are those where the change in charge is small, there are no emitted α -particles from the incident nucleus, and there are no black or grey tracks due to evaporation fragments from the target nucleus, i.e. stars of the type $0 + \mathcal{V}\mathcal{H} + n_s$. Such events will be particularly difficult to detect for $\mathcal{V}\mathcal{H}$ -nuclei, since a small change of charge on such a track is much less easily recognizable than it would be on the track of a nucleus of lower charge. As a consequence an indication of whether

any missing has occurred can be obtained by comparing the N_h distribution observed in this experiment with that observed previously for M -nuclei, Fowler *et al.* (1957), Rajopadhye and Waddington (1958), fig. 1. The significance of the lack of interactions with $N_h=0$ apparent from this comparison is enhanced when it is remembered that according to the accepted cross sections M -nuclei will make only 10% of their interactions with the hydrogen in emulsion, whereas the $\mathcal{VH}$ -nuclei will make 15%. Thus the relative number of $N_h=0$ interactions might be expected to be greater for $\mathcal{VH}$ -nuclei than for M -nuclei, the opposite to what is actually observed. It seems therefore that there has been a bias against finding interactions of the type with $N_h=0$.

The magnitude of these detection losses can be estimated, although not in a very statistically significant manner, in the following way:

- (i) A lower limit can be obtained by considering the number of interactions with the hydrogen in emulsion that should be observed among those produced by $\mathcal{VH}$ -nuclei. About 27 of the 174 interactions in this sample could be expected to be with hydrogen, whereas only 26 which could possibly be such interactions were observed. Thus it is just feasible that no interactions at all were missed.
- (ii) An upper limit can be obtained from a comparison with the interactions produced by M -nuclei. Of these some 10% resemble, but are not, interactions with hydrogen. The proportion of these spurious hydrogen interactions among the $\mathcal{VH}$ -nuclei should not be greater, and thus an upper limit to the number of missed interactions is about 20.
- (iii) Another estimate of the upper limit can be obtained from the observed value of the mean free path. In order for this to have been 29.4 g/cm^2 , the predicted value, 23 interactions must have been missed.

In the light of these considerations it has been decided to assume, arbitrarily, that the loss of interactions amounted to 15 ± 5 , all of the type $0 + \mathcal{VH} + n_s$.

3.2. Fragmentation Parameters

Table 3(a) shows the fragmentation parameters, P_{ij} , observed in emulsion, both for the case where no correction is made for detection losses, and for that where a correction of the amount assumed above is made. Similar figures are given for those interactions which have $N_h \leq 7$. Table 3(b) shows the results obtained when the data of this experiment are combined with those published previously, Fowler *et al.* (1957), Cester *et al.* (1958), Puschel (1958) and Rajopadhye and Waddington (1958). A study of these other experiments suggests the presence of a detection loss similar to that observed in this experiment, and thus a correction of 21 ± 7 interactions was applied to the combined data.

Since the fragmentation parameters for $\mathcal{H}$ -nuclei have not been determined in this experiment, it has been necessary to extract them from the published data, and their values are shown in table 3 (c). Considerations of the N_h distribution, and of the mean free path obtained for these nuclei, do not suggest any serious failures to detect interactions. This can be explained when it is remembered that such nuclei have a much lower mean charge, $\bar{Z} \sim 12$, cf. $\bar{Z} \sim 25$ for $\mathcal{V}\mathcal{H}$ -nuclei, and thus interactions resulting in a small change in charge are much easier to detect, so that detection losses should be small.

Table 3. Fragmentation Parameters of $\mathcal{V}\mathcal{H}$ -nuclei:
Corrected Values shown in Brackets

(a) As observed in this experiment					
	$\mathcal{V}\mathcal{H}$	$\mathcal{H}$	M	L	α
All	0.12 ± 0.03	0.33 ± 0.05	0.12 ± 0.03	0.18 ± 0.03	1.54 ± 0.16
$N_h \leq 7$	(0.18 ± 0.04) 0.18 ± 0.04 (0.26 ± 0.06)	(0.31 ± 0.05) 0.43 ± 0.08 (0.38 ± 0.07)	(0.11 ± 0.03) 0.14 ± 0.04 (0.17 ± 0.03)	(0.17 ± 0.03) 0.22 ± 0.05 (0.20 ± 0.04)	(1.40 ± 0.14) 1.63 ± 0.20 (1.42 ± 0.18)
(b) Results from all experiments					
All	0.12 ± 0.02	0.34 ± 0.04	0.13 ± 0.02	0.17 ± 0.03	1.51 ± 0.13
$N_h \leq 7$	(0.19 ± 0.03) 0.15 ± 0.03 (0.26 ± 0.05)	(0.31 ± 0.04) 0.41 ± 0.06 (0.36 ± 0.06)	(0.12 ± 0.02) 0.13 ± 0.03 (0.11 ± 0.03)	(0.16 ± 0.03) 0.18 ± 0.04 (0.16 ± 0.04)	(1.38 ± 0.11) 1.55 ± 0.17 (1.34 ± 0.15)
(c) Fragmentation parameters of $\mathcal{H}$ -nuclei, uncorrected for any loss					
	$\mathcal{H}$	M	L	α	
All	0.11 ± 0.02	0.29 ± 0.04	0.17 ± 0.03	1.18 ± 0.13	
$N_h \leq 7$	0.15 ± 0.04	0.41 ± 0.08	0.20 ± 0.05	1.32 ± 0.18	

§ 4. DISCUSSION

It has been generally assumed that the fragmentation parameters obtained from those interactions in emulsions which have $N_h \leq 7$ are upper limits to the values applicable for air, Rajopadhye and Waddington (1958), Lorchmann and Teucher (1959), Cester *et al.* (1958). While the validity of this assumption has been contested, it will be accepted in this discussion. However, in order to verify that no gross errors are introduced, absolute limits to these maximum parameters will also be established.

The interaction mean free paths in air have been calculated from eqn. (1), and in view of the considerable evidence supporting the validity of this equation can hardly be seriously in error. Thus, using these mean

free path values, and the corrected fragmentation parameters for $N_h \leq 7$, it is possible to calculate the extrapolation of an observed charge distribution from a point of observation within the atmosphere, to the top of the atmosphere. For example, with $R = 0.35$ and a ratio of $\mathcal{V}\mathcal{H}/\mathcal{H}$, $S = 0.24$ at 12 g/cm^2 , Hillier and Rajopadhye (1958), the calculated value of R_0 was 0.41 . This value may be compared with that of $R_0 = 0.43$ found from the same data when H -nuclei are not separated into two groups, but considered as a whole.

A number of assumptions have to be made in this calculation. These will now be considered.

(i) Sensitivity of R_0 on the ratio S . When all the available data on the relative abundances of these nuclei are gathered together, Waddington (1960), S appears to have a value of 0.23 ± 0.03 at a depth in the atmosphere of about 14 g/cm^2 . R_0 should vary with S , but is not very sensitive to small changes. For example, even if the true value of S is as low as 0.17 , a fluctuation of two standard deviations, R_0 is only lowered from 0.41 to 0.40 .

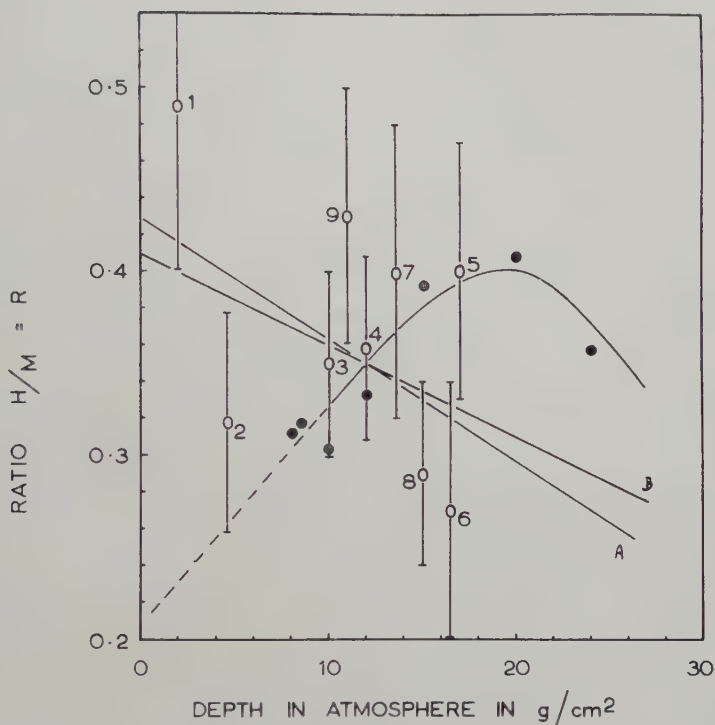
(ii) Fragmentation parameters in air. The assumption that the overall effect of those interactions in emulsions with $N_h \leq 7$ is similar to that produced in air is not easily justified. However, it is possible to obtain a lower limit for the extrapolated value of R by making extreme assumptions in the derivation of the fragmentation parameters. For R_0 to be a lower limit, $P_{\mathcal{V}\mathcal{H},\mathcal{V}\mathcal{H}}$, $P_{\mathcal{V}\mathcal{H},\mathcal{H}}$ and $P_{\mathcal{H},\mathcal{H}}$ must take maximum values, while $P_{\mathcal{V}\mathcal{H},M}$ and $P_{\mathcal{H},M}$ take minimum values. From the emulsion data these limiting values can be obtained in the following manner. Since all the interactions with those nuclei in emulsion which resemble those in air must have $N_h \leq 7$ it may be assumed that all the observed fragments produced from such interactions do come only from the air-like nuclei. Since the abundance of these nuclei in emulsion is known, the relative number of $N_h \leq 7$ interactions due to air-like target nuclei can be calculated. Thus the extreme upper limits for these fragmentation parameters are $P_{\mathcal{V}\mathcal{H},\mathcal{V}\mathcal{H}} \leq 0.50$, $P_{\mathcal{H},\mathcal{H}} \leq 0.70$ and $P_{\mathcal{H},\mathcal{H}} \leq 0.40$. Notice that this procedure implies that no $\mathcal{V}\mathcal{H}$ or $\mathcal{H}$ fragments are produced by interactions with the hydrogen in emulsion nor by peripheral collisions with heavy nuclei. From the emulsion data $P_{\mathcal{V}\mathcal{H},M}$ and $P_{\mathcal{H},M}$ can be allowed to tend to zero. Using these values an R of 0.35 at 12 g/cm^2 gives $R_0 \geq 0.31$. Thus, even by making these extreme assumptions it is hardly possible to allow R_0 to be as low as Appa Rao *et al.* claim.

(iii) Mean free paths in air. The values taken depend on eqn. (1) the validity of which has been discussed in § 3.1, from which it appeared that these values can hardly be seriously in error. Furthermore, R_0 is not very sensitive to small changes in these values.

(iv) The constancy of the mean mass in the $\mathcal{V}\mathcal{H}$ and $\mathcal{H}$ groups of nuclei. While it is not possible to calculate the change in the mean mas_S introduced by passage through 12 g/cm^2 of atmosphere precisely, due

to a lack of knowledge of the necessary parameters, it is possible to show that this change must be small. For example, consider an incident $\mathcal{VH}$ -group composed of 50% Fe and 50% Ca, with $\bar{A}=48$, and assume $P_{\text{Fe,Ca}}=0.30$. Then passage through 12 g/cm² will result in a group of 42% Fe and 58% Ca with $\bar{A}=46.7$. Similarly, consider an incident

Fig. 2



The variation of the ratio R in the atmosphere. Points shown as $\bullet$ are due to Appa Rao *et al.* (1958), while the other experimental points are : 1. Yagoda (1958) ; 2. Freier *et al.* (1959) ; 3. Koshiba *et al.* (1958) ; 4. Waddington (1957) ; 5. Cester *et al.* (1958) ; 6. Waddington (1958) ; 7. Jain *et al.* (1959) ; 8. Von Friesen *et al.* (1959) ; 9. Biswas *et al.* (1959). These last two points are stated by the authors to be preliminary. Also shown are the diffusion growth curves calculated without separating the H -nuclei into two groups, A ; and by separating them into $\mathcal{VH}$ and $\mathcal{H}$ -nuclei, B ; both normalized to $R=0.35$ at 12 g/cm². The growth curve constructed by Appa Rao *et al.* (1958) is also shown, with the least extreme extension to 0 g/cm² shown as a dashed line.

$\mathcal{H}$ -group composed of 70% Ne, 30% S with $\bar{A}=23.6$ and assume $P_{\mathcal{VH},S}=P_{\mathcal{VH},Ne}=P_{S,Ne}=0.20$. Then passage through 12 g/cm² will result in a group of 31% S, 69% Ne with $\bar{A}=23.7$. Thus it appears that the assumption of constant mean mass in these two groups cannot be seriously incorrect for transmissions through reasonable amounts of matter.

The available experimental data on the values of R obtained in a number of experiments are shown in fig. 2, where R is plotted against the depth in the atmosphere. Also shown are the two diffusion growth curves for H -nuclei and for VH plus H -nuclei, arbitrarily normalized to $R=0.35$ at 12 g/cm^2 , and the growth curve determined by Appa Rao *et al.* Notice that in fact these diffusion curves should not be quite linear, but are drawn so for convenience, and that due to the arbitrary normalization they may be shifted parallel to themselves. The spread of the experimental values, and their concentration in the region where the values of R predicted by the various curves are closely similar, makes it difficult to draw any firm conclusions from these data, although they appear to fit the diffusion curves somewhat better than those of Appa Rao *et al.*

§ 5. CONCLUSIONS

From the above analysis it appears difficult to accept the value of R_0 predicted by Appa Rao *et al.*, and it would seem that the best value of R_0 available at this time is $R_0=0.38 \pm 0.04$, where the uncertainty is mainly due to the difficulty of normalizing the diffusion growth curves.

This figure may be compared with those calculated from the cosmic abundances determined by Cameron (1959) and Suess and Urey (1956) of 0.1 and 0.37 respectively. The difference between these figures is almost entirely due to the uncertain abundance of ^{20}Ne , but the true value probably lies within these limits. Thus it can be seen that, if account is taken of the degradation in mass produced by passage through the interstellar material between the source and the earth, the cosmic radiation is anomalously rich in heavy nuclei. It must be concluded, therefore, that either the source of this radiation is a region with an abundance of heavy elements which is greater than normal, or the acceleration mechanism preferentially accelerates heavy nuclei. This conclusion would not follow if R_0 was appreciably lower than the value obtained here.

ACKNOWLEDGMENTS

The author is grateful to Professor C. F. Powell, F.R.S., for the facilities of his laboratory, and to the Royal Society for the award of a Mackinnon Research Studentship. The existence of sufficient experimental material in this laboratory to permit this investigation was first pointed out by Dr. P. H. Fowler, while Dr. M. W. Friedlander very kindly arranged for the exposure of the T-stack in Texas. Finally the contribution of the observing staff of this laboratory must be acknowledged with deep gratitude.

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The Observation of Sharp Internal Friction Peaks in Beryllium†

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[Received October 27, 1959]

ABSTRACT

Measurements have been made as a function of strain and temperature with specimens of commercially pure beryllium. Very sharp internal friction peaks were observed which are similar to those reported as occurring in aluminium. The previously suggested mechanism giving rise to these maxima is discussed in terms of the evidence obtained here.

§ 1. INTRODUCTION

THE brittleness of beryllium is the major drawback to its extensive use in nuclear reactors and in other fields. It has low neutron absorption, low density and a high modulus of elasticity which are all very attractive properties, but in its present commercial form the metal is brittle and fabrication is difficult. It has been suggested that impurities in beryllium are responsible for its brittle behaviour but no one has yet been able to produce very pure beryllium to test this point directly.

Internal friction measurements provide a very sensitive test for the study of dislocations and their interaction with impurity atoms. This interaction determines to a large extent the mechanical properties of the metal. Granato and Lücke (1956) have developed a dislocation-pinning point model that can be compared quantitatively with internal friction data and it was hoped by this means to obtain information about the behaviour of impurities in beryllium. The main result of the experiments was the observation of very sharp internal friction peaks as the specimen temperature was changed. Similar peaks have been observed in aluminium (Birnbaum and Levy 1956, Filmer *et al.* 1958) and the mechanism which is suggested to be the cause of the internal friction peaks is discussed in relation to the evidence obtained in these experiments.

§ 2. APPARATUS

The apparatus used in these experiments is described fully elsewhere (Dickson and Strauch 1959). A specimen in the form of a cylindrical rod 20 cm long and 6 mm diameter was clamped at its mid-point and set into longitudinal oscillation. The internal friction was determined from the rate of decay of the oscillations when the driving force was switched off. Mechanical oscillations of the rod were induced and detected

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electrostatically. An electrode was placed close to each end of the specimen and biased with a d.c. voltage relative to the specimen. Application of an oscillatory voltage to one of the electrodes at the resonant frequency of the specimen induced the mechanical vibrations. The other electrode formed part of a condenser microphone which produced a signal whose amplitude was directly proportional to the amplitude of oscillation of the beryllium rod. The detection electrode was connected through a phase shifter and amplifier to the driving electrode and when this circuit was completed it formed a regenerative loop in which the oscillations built up from noise levels. The advantages of this circuit were that specimens having a very low internal friction could be maintained at a fixed amplitude of oscillation indefinitely and a precise determination of the resonant frequency of the specimen was possible.

The internal friction could be measured in the strain range 10^{-6} to 10^{-8} . A film record was made of the decaying signal from the detecting electrode and by measuring the time taken for the oscillations to decay through a small amplitude range at selected points on the film record the variation of internal friction with strain could be determined. The internal friction coefficient, ϕ , is given by $\phi = (1/\pi ft) \log_e (A/B)$ in which f is the frequency of the oscillations and t the time for them to decay from amplitude A to amplitude B . In all these experiments the frequency of the oscillations was ~ 30 kc/s. Where the internal friction was found to be independent of strain amplitude a stop watch was used to measure the time interval in a strain range such that $A/B = 10$.

The specimen was enclosed in a stainless steel container evacuated to a pressure of 10^{-5} mm Hg. The temperature control system was of the saturable reactor type providing continuous regulation of the heat supply to the furnace and its stability allowed measurements to be made at intervals of 0.25°C .

§ 3. SPECIMENS

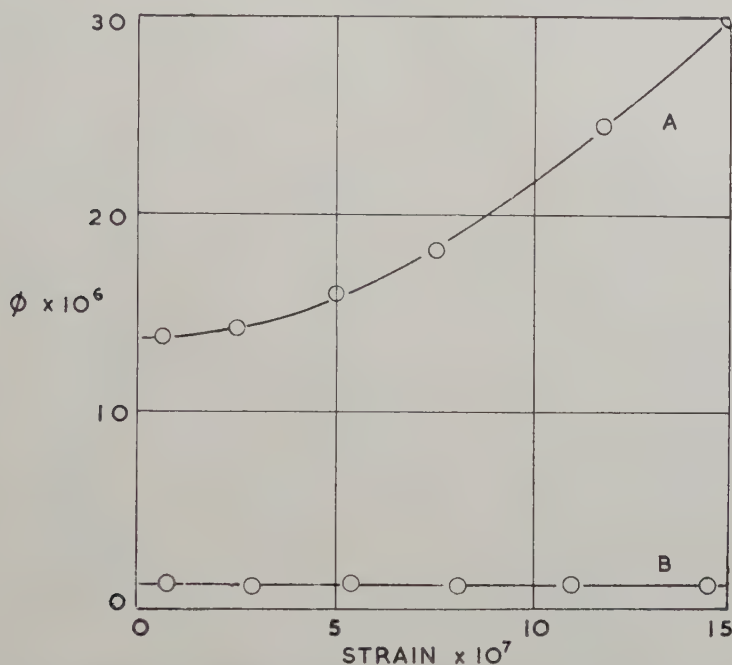
The rods were supplied by the Brush Beryllium Corporation and were QMV grade. They had been manufactured by the warm extrusion of a hot pressed powder billet and the grain size was 0.02 mm. The chemical analysis provided by the manufacturers showed the major impurities to be BeO 1.16%, Al 0.15%, Fe 0.1%, Mn 0.013%, Ni 0.01%. Smaller amounts of Ag, Cd, Co and Li were also present. The density, ρ , of each rod was measured and found to be $1.847 < \rho < 1.852$ g/cm³. This is greater than the theoretical density of 1.848 g/cm³ calculated on the basis of the lattice constants because of the presence of the impurities. The texture of the rods was not determined but it is well known that rod extrusion produces a fibre texture in which most of the grains have their c axis perpendicular to the rod axis (Kaufmann *et al.* 1950).

The only specimen preparation carried out was mechanical polishing of the ends of the rods so that they were plane and perpendicular to the longitudinal rod axis.

§ 4. EXPERIMENTAL RESULTS

From measurements of the resonant frequency, density and dimensions of each of the nine specimens the velocity of sound in beryllium, v , was calculated and found to be $1.26 \times 10^6 < v < 1.27 \times 10^6$ cm/sec and the dynamic Young's modulus E , $2.89 \times 10^{12} < E < 2.94 \times 10^{12}$ dynes/cm². These measurements were made at room temperature and show good agreement with the results of Overton (1950), $v = 1.26 \times 10^6$ cm/sec and Gold (1950), $E = 2.965 \times 10^{12}$ dynes/cm².

Fig. 1



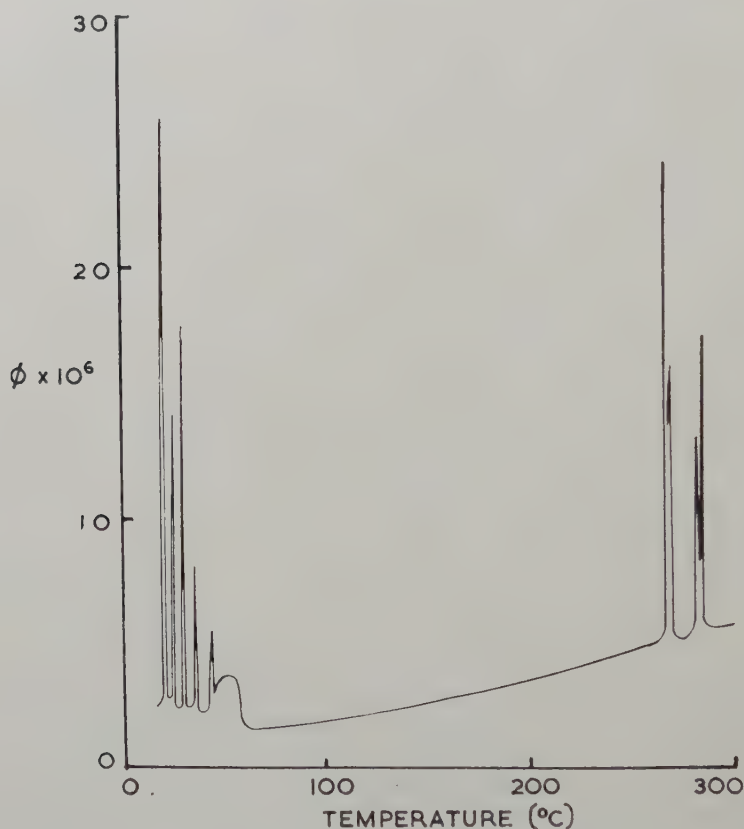
Strain dependence of internal friction. Specimen in 'as received' condition, curve A, and after three-hour anneal at 500°C, curve B.

All the specimens in the 'as received' condition showed a strain dependence of the internal friction at room temperature as illustrated in fig. 1, graph A. The internal friction became independent of strain after a three-hour anneal at 500°C, fig. 1, graph B. It is generally known that, especially with single crystals, the work done on the specimen during mounting in the apparatus can increase the measured values of the internal friction. To check this point one specimen was removed from and remounted in the apparatus three times. The results obtained on each occasion were in agreement within the experimental error of 5%. From this it was concluded that the observed effect was genuine. The elimination of the strain dependence of the internal friction could be due to the

segregation of impurities to dislocations. However, attempts to prove this point and determine the kinetics by quenching and ageing experiments were not successful due to the high sensitivity of the internal friction to temperature under certain circumstances.

In a first attempt to measure the temperature dependence the specimen used was that which had previously been annealed for three hours at 500°C and the readings, taken every 10°C, showed a much larger scatter than

Fig. 2

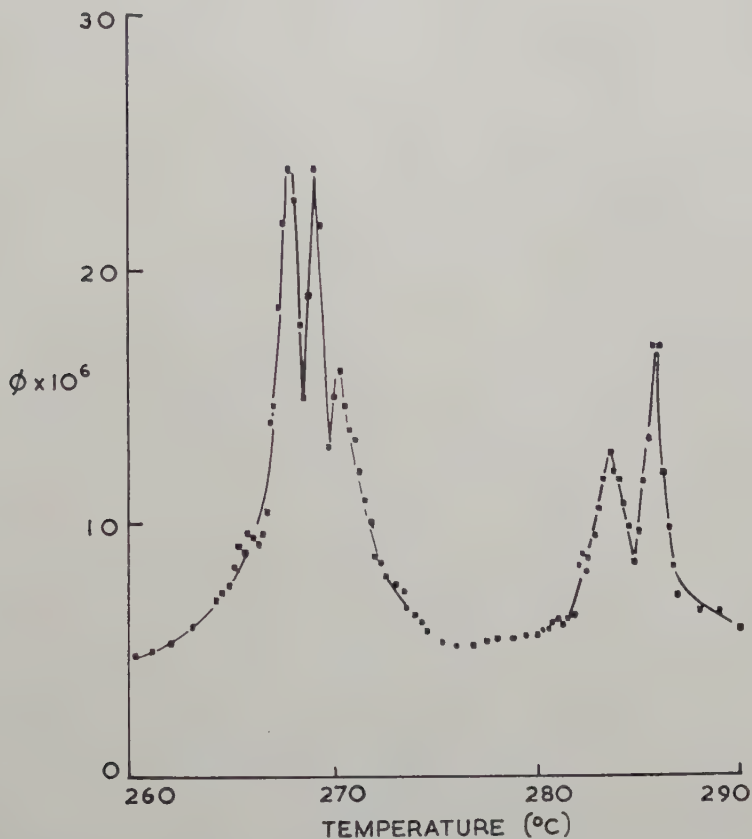


Temperature dependence of internal friction after three-hour anneal at 500°C.

could be attributed to experimental error. More careful measurements were then taken at intervals of 0.25°C as the beryllium rod was cooled down from 300°C at approximately 5°C per hour. The results, fig. 2, show the existence of some very sharp internal friction peaks in the temperature ranges 20–60°C and 260–290°C. Part of this graph is shown on a larger scale in fig. 3 in which all the experimental points are plotted. The experiment was repeated several times in the temperature range 20–50°C

and the major peaks were found to be reproducible on both heating and cooling cycles. The internal friction values as plotted were calculated from the time taken for the oscillations to decay by a factor of ten in amplitude and represent the average internal friction in the strain range 10^{-6} to 10^{-7} . Film records of the decay taken at various temperatures, including the tops of the sharp peaks, showed no strain dependence of the internal friction. The maximum strain in the specimen during these experiments did not exceed 1×10^{-6} .

Fig. 3

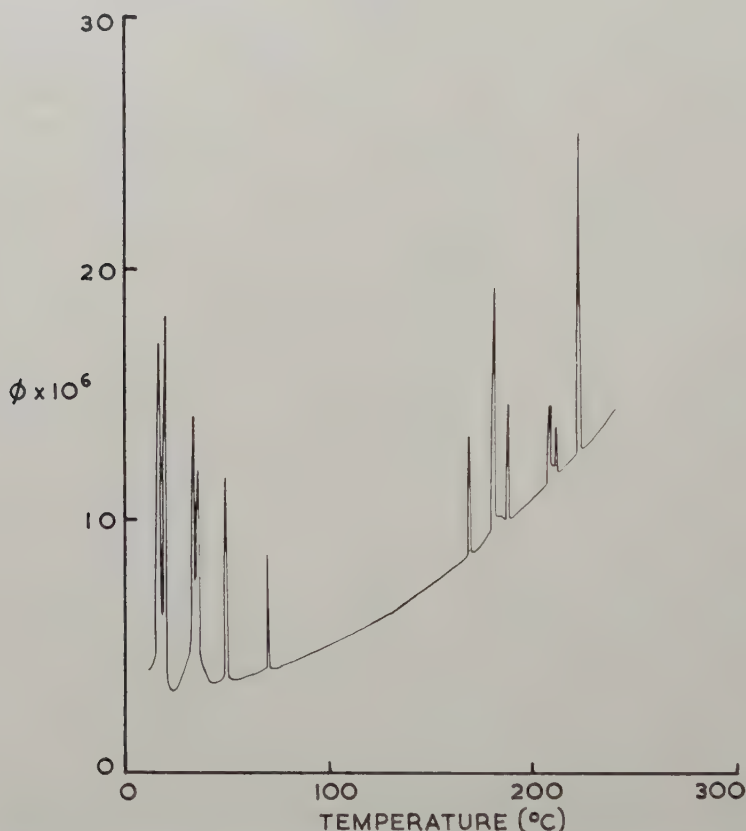


Detail of some of the sharp internal friction peaks shown in fig. 2.

A second specimen was mounted in the apparatus and annealed *in situ* for 20 hours at 235°C . Measurements of the internal friction which were taken as the specimen was slowly cooled to room temperature are shown in fig. 4. Sharp peaks similar to those shown in fig. 2 were observed near room temperature and in the temperature range 170 – 230°C . After a further anneal *in situ* for 50 hours at 350°C measurements were again made as the rod was slowly cooled to room temperature. The background internal

friction was reduced by this heat treatment as shown in fig. 5 and the sharp peaks were now observed in a broad temperature region extending from 30–160°C. When this specimen was further heated to 300°C and furnace cooled to room temperature, the cooling rate being 200°C per hour at 300°C, only two small peaks at 30°C and 50°C were observed between room temperature and 70°C. It was again found that the internal friction in

Fig. 4



Temperature dependence of internal friction. Specimen in 'as received' condition annealed for 20 hours at 235°C before measurements made.

this temperature range was repeatable on both heating and cooling. Finally a very slow cool from 300°C produced sharp peaks once more in this low temperature region.

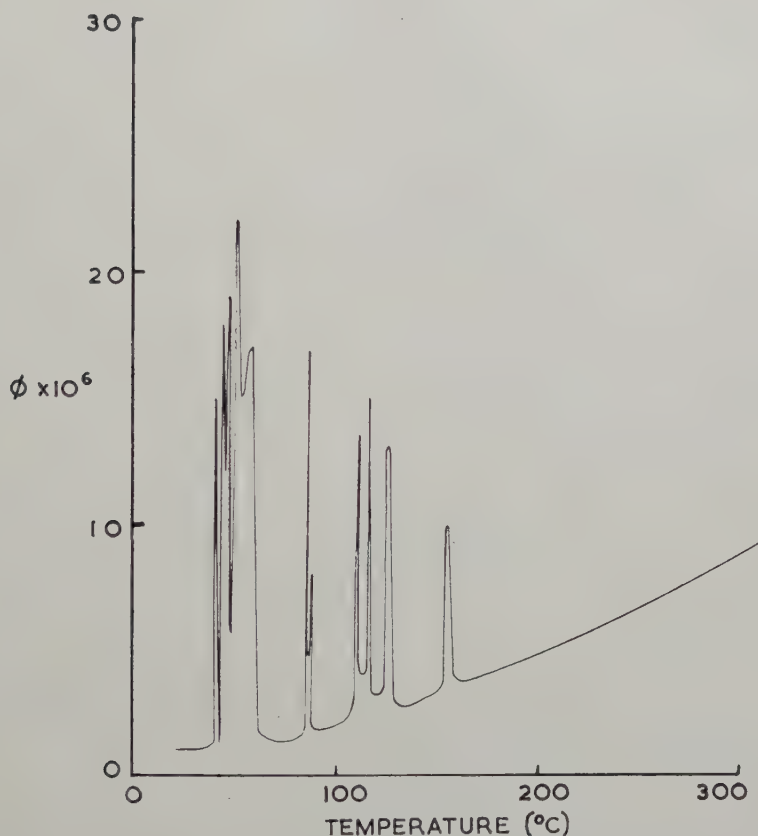
All these observations were made without removing the beryllium rod from the apparatus. Since it was found possible to alter the temperature region in which the sharp peaks were observed and also to repeat the measurements made during cooling and heating cycles in the range 20°C

to 70°C it is thought that they were due to energy absorption by the specimen and not energy losses in the apparatus. When the apparatus was used with specimens of other metals these effects were not observed.

§ 5. DISCUSSION

The very low values of internal friction, $\phi = 1 \times 10^{-6}$, were probably due to the highly preferred orientation of the polycrystalline specimens. In this experiment the shear stress is a maximum on planes at 45° to the

Fig. 5



Temperature dependence of internal friction. The specimen used to obtain the results shown in fig. 4 was annealed for 50 hours at 350°C prior to these measurements.

longitudinal specimen axis and is very small across the basal planes of the individual grains since their c axis is perpendicular to the specimen axis. Dislocations can only be moved by a shear stress and thus the dislocation movement in the basal plane, which is the primary slip system at the temperatures involved, is very small. The effect of crystallographic

orientation on internal friction has been demonstrated by Read (1941) using specimens of zinc.

Quenching and ageing experiments were carried out and there was some evidence that impurities were put into solution and then segregated to the dislocations, pinning them and so reducing the internal friction. These results were not satisfactory because of the irregular nature of the temperature dependence of the internal friction.

Sharp internal friction peaks very similar to those reported here have been observed with single crystal specimens of aluminium by Birnbaum and Levy (1956) and by Filmer *et al.* (1958) who used polycrystalline aluminium. Birnbaum and Levy attributed the sudden changes in internal friction to 'avalanches' of dislocations freed by the oscillating stress from loose pinning joints. Filmer *et al.* pointed out however that the freed dislocations must have moved to another stable configuration in order to produce a peak in the internal friction results and not a step.

This explanation of the phenomenon can be tentatively applied to the results on beryllium. However, the fact that the peaks were repeatable on heating and cooling cycles shows that the mechanism must be reversible. On the basis of the previously proposed model this fact implies that several pinning point configurations are possible on the dislocation lines and each configuration is stable in a particular temperature zone. As the temperature of the specimen is changed from one of these zones to another the dislocations are freed at the transition temperature and their increased mobility produces high values of internal friction. The position of the internal friction peaks on the temperature scale and their magnitude were altered by heat treatment at temperatures in excess of 150°C. This evidence is in agreement with the results on polycrystalline aluminium where it was found possible to eliminate some of the peaks and reduce the magnitude of others by annealing the specimen for 11 hours at 60°C.

If the internal friction peaks are due to the freeing of dislocations from pinning points whose energy is precisely defined then each observed internal friction peak would characterize a particular type of pinning point. The multiplicity of the peaks observed in these experiments and the variation in the temperature ranges in which they occur makes a mechanism of this type less feasible.

The evidence obtained here that the internal friction was independent of strain in the neighbourhood of the maximum values recorded implies that if the effect is due to dislocation breakaway the pinning points concerned are completely ineffective under these particular experimental conditions. The dislocation loops are not re-pinned at the zero point of the stress cycle. Considering the equation proposed by Granato and Lücke (1956) the strain independent internal friction is proportional to L^4t where L is the average length of dislocation loop which vibrates under the action of the applied oscillatory stress and t is a factor which depends on the distribution of loop lengths assumed. The magnitude of the internal friction peaks could be accounted for by an increase of a factor of two

in the average loop length. An alternative explanation could be based on the factor t . As stated by Granato and Lücke (1957), $t=1$ when the pinning points are equispaced along the dislocation lines and when they are randomly distributed $t=120$. A disturbance of the distribution of pinning points could give rise to an internal friction peak. However, it is difficult to visualize a mechanism whereby the distribution of pinning points could be suitably disturbed on all the active dislocations simultaneously.

An alternative interpretation of the lack of strain dependence of the internal friction is that the sharp peaks were due to a relaxation process. Some of the peaks do have a shape consistent with a process of this type but the activation energy calculated from the shape of the peak is extremely high and far in excess of the sublimation energy of beryllium. A relaxation process should be accompanied by a change in the resonant frequency of the specimen. This was not observed in these experiments where the accuracy of frequency measurements was only $\pm 0.4\%$.

There is clearly a need for much more experimental evidence before a satisfactory explanation for the occurrence of the sharp internal friction peaks is obtained. It is for this reason that the results obtained in this investigation have been reported in full detail.

ACKNOWLEDGMENTS

I would like to thank Dr. T. P. Hughes for his interest and encouragement in this work and the Chairman of Tube Investments Ltd. for permission to publish this paper.

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Ferromagnetism in Pd-rich Palladium-Iron Alloys†

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[Received January 12, 1960]

ABSTRACT

Ferromagnetism has been detected in disordered solid solution alloys of Fe in Pd at compositions down to 1.25 atomic % of iron. Data are presented on magnetic moments and on Curie points. It is shown that part of the observed magnetic moment must be associated with the Pd atoms, and cannot be completely localized on iron atoms.

§ 1. INTRODUCTION

ACCORDING to the phase diagram of the alloy system palladium-iron published by Hansen (1958), a continuous region of solid solution having the face-centred cubic structure exists over the whole composition range at high temperatures. At lower temperatures the face-centred cubic phase is still stable between 0 and 60 atomic % of iron but there are two superlattice structures, centred round the FePd and FePd₃ compositions respectively.

Fallot (1938) showed that both these superlattices are ferromagnetic, with Curie points of about 750°K for FePd and about 530°K for FePd₃. Also, he showed that the disordered face-centred cubic structure obtained by quenching from high temperatures (and so suppressing the formation of the superlattices) is ferromagnetic down to not more than 12 atomic % of iron.

In view of the interest inherent in the question of whether long-range interactions between magnetic iron atoms in a non-magnetic palladium matrix are alone responsible for the ferromagnetic state, and whether palladium atoms themselves contribute any magnetic moment, it seemed desirable to extend and improve upon Fallot's measurements.

After the present work had been started, Gerstenberg (1958) published measurements on the paramagnetic susceptibility of PdFe alloys containing 1, 3, 5 and 7 atomic % of iron. In all cases the Curie-Weiss law was obeyed, and the extrapolated paramagnetic Curie point was positive. This implied that ferromagnetism persisted down to 1% of iron.

§ 9. PREPARATION OF THE ALLOYS

A series of five alloys containing 1-16 atomic % of iron was prepared from pure palladium lent by the Mond Nickel Company, and Johnson-Matthey spectrographic iron. The preparation was by melting in an

† Communicated by Professor W. Sucksmith, F.R.S.

argon arc furnace. The negative electrode of a direct current arc was a water-cooled tungsten rod and the positive electrode consisted of the specimen to be melted, which rested on a water-cooled copper base. Mostly the alloys weighed 2–3 g. All the compositions were chosen so as to lie outside the range of superlattice stability.

The alloys were analysed chemically for the iron content and spectrographically for the presence of significant impurities. The compositions are given in table 1. The probable error in atomic percentages is $\pm 0.05\%$. All the alloys contained spectrographic traces of silver and copper, and that with 1.25% of iron had also a similar trace of silicon.

Table 1

Iron content, atomic %	1.25	3.16	5.11	9.78	15.75
σ_0 , c.g.s. units/g	4.9	13.1	18.8	31.9	45.3
Bohr magneton number p	0.093	0.246	0.350	0.581	0.800
Curie point θ , °K	66	122	162	236	377

§ 3. MAGNETIC TECHNIQUES

Intensity of magnetization in strong fields was measured as a function of temperature and of field in a Sucksmith ring balance (Sucksmith 1939). The magnetization at room temperature of BISRA pure iron 'AH', to which the absolute data of Weiss and Forrer (1926) were assumed to apply, was used as a standard to which other measurements could be referred. Magnetic isothermals were obtained for a range of eight applied fields between 4 and 13 kilo-oersteds, at temperatures down to a minimum of about 20°K and up to the respective Curie temperatures.

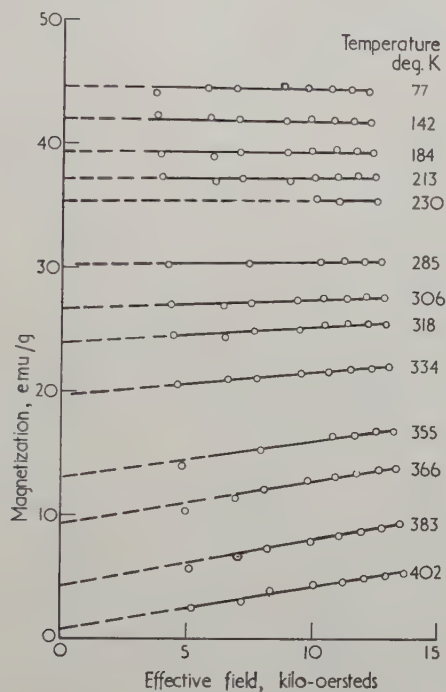
Above room temperature, a small evacuated electric furnace was attached to the balance. At lower temperatures, the specimen mount was enclosed by a metal tube, in which a high vacuum could be maintained. This tube was in turn surrounded by a shaped Dewar vessel capable of containing either liquid nitrogen or liquid hydrogen. The specimen was mounted inside the balance at the end of a thin-walled tube of silica, and its rate of heat transfer with the surroundings was small. Thus it was usually possible to make the measurements at selected temperatures below room temperature while the temperature was drifting slowly. More rapid changes of temperature were achieved by the temporary admission of helium at low pressure.

Temperatures were measured by means of a thermocouple of 'Pallador', placed in good thermal contact with the specimen.

§ 4. RESULTS

Spontaneous magnetizations σ_T at the various temperatures T were estimated by plotting the magnetization against the effective field (corrected for demagnetizing factor) at constant temperatures, and extrapolating their linear parts to the magnetization in zero field. An example of a set of these magnetic isothermals, for the 15.8% alloy, is given in fig. 1. Their general form is not unlike that found (Weiss and Forrer 1926) in say,

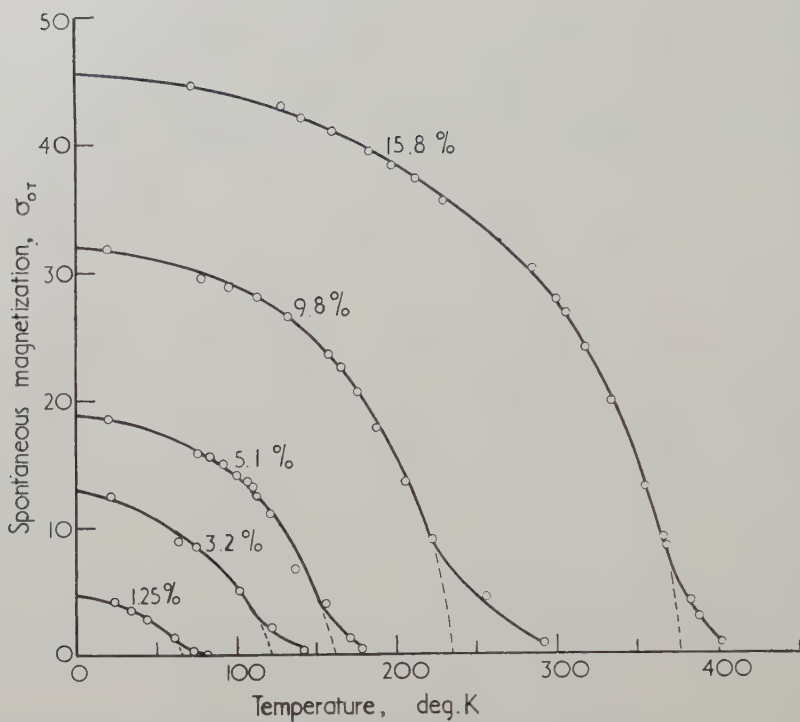
Fig. 1



Magnetic isotherms for the 15.8 atomic % Pd-Fe alloy.

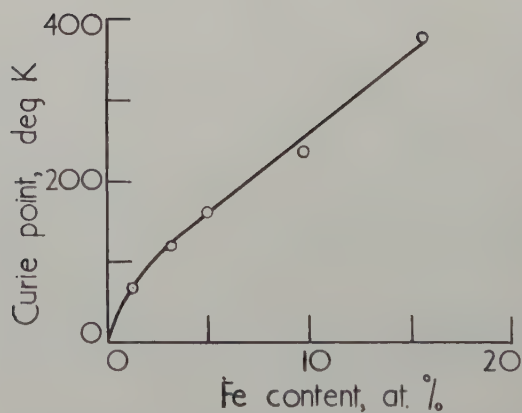
nickel, and in this respect the alloys seem to show normal ferromagnetic behaviour. The values of σ_T obtained are plotted as a function of temperature for each of the present alloys in fig. 2. The spontaneous magnetizations σ_0 at zero temperature were estimated by drawing the linear parts of graphs of σ_T against T^2 to where $T^2 = 0$. Values of σ_0 were converted to Bohr magneton numbers p , assuming the magnetic moment of the Bohr magneton to be 5586 c.g.s. units per gram molecular unit (table 1). The respective Curie points were found by plotting σ_T against T and extrapolating the part with steepest slope to the temperature axis. They are plotted against composition in fig. 3.

Fig. 2



The variation of spontaneous magnetization with temperature for Pd-Fe alloys.

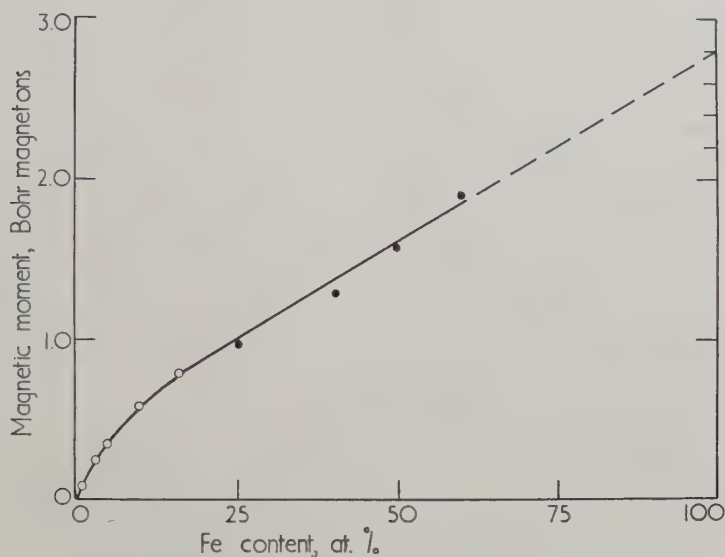
Fig. 3



The variation of Curie point with iron content.

The magneton numbers of the present alloys and also those of Fallot's alloys are shown in fig. 4.

Fig. 4



Bohr magneton numbers plotted against iron content. The open points are present measurements; the black ones are due to Fallot (1938).

§ 5. DISCUSSION

The first remarkable feature of the measurements is that ferromagnetism persists down to such low iron contents. In fig. 3, the Curie point of the alloys appears to extrapolate to zero at zero iron concentration; and at 1.25% of iron the Curie point has already risen to over 60°K.

Sato *et al.* (1959) have theoretically demonstrated how, when ferromagnetic ordering arises from nearest-neighbour interactions between magnetic atoms dissolved in a non-magnetic matrix, the Curie point remains zero and no ferromagnetic state occurs until a finite concentration C_0 of the magnetic solute is attained. Their estimate of C_0 was of the order of $1/z$, where z is the coordination number of the crystal structure. Thus for a face-centred cubic structure ($z=12$), C_0 should be of the order of 8%, agreeing with the experimental observations in Au-rich gold-iron solid solutions (Kaufmann *et al.* 1945), where ferromagnetism does start at about 8 atomic %. Thus it appears that in the most dilute Pd-Fe alloys the ferro-magnetism cannot be a result of only nearest neighbour interactions between iron atoms. Some longer-range mechanism must be active.

The second remarkable feature of the observations concerns the magnitude of the magnetic moments. The dependence of measured magnetic moment on applied field, as typified by fig. 1, introduces little uncertainty

(especially at low temperatures) into the estimates of the values of the spontaneous magnetization σ_T : the spontaneous magnetization varies regularly with temperature (fig. 2) and there is little room for doubt in the estimation of its value σ_0 at $T=0$. Yet if we suppose that the whole of the magnetic moment p shown for each alloy in table 1 is located on iron atoms, we find that the moment per iron atom would be as shown in table 2.

Table 2

Fe content, atomic %	1.25	3.16	5.11	9.78	15.75
Ratio $\frac{\text{Total magnetic moment}}{\text{iron content}}$	7.4	7.8	6.9	5.9	5.1

The experimentally observed magneton number p is related to the difference n between the numbers per atom of electrons with positive and negative spin by $p = \frac{1}{2}g.n$, where g is the spectroscopic splitting factor. Experimental g values are not available for these alloys. But in pure iron, g is about 2.1 (see Bagguley and Owen 1957). Thus taking this value for g , we must infer that the values given in table 2 require that there should be a difference between the numbers of electrons with positive and negative spin of up to about seven per iron atom. This is clearly impossible in either an atomic $3d$ level or a $3d$ band in which the Pauli exclusion principle dictates that vacancies can exist for only five electrons per atom with positive and five with negative spin.

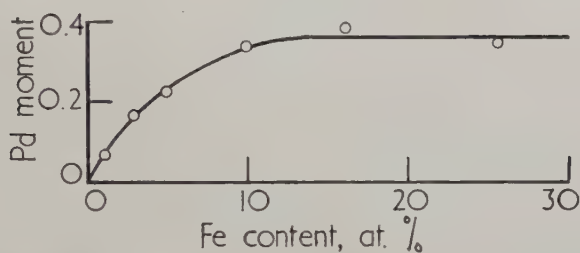
We must therefore conclude that some of the magnetic moment which is present is not located on iron atoms. The present observations give no direct information beyond this on the question of the source of the magnetic moment in the alloys.

It is useful to discuss these alloys in terms of a model in which there is some characteristic localization of magnetic moment on each of the kinds of atom present. Wohlfarth (1954, 1956) has extended the simplified collective electron theory of ferromagnetism to the related alloys of palladium containing nickel or cobalt in solution. He discussed the alloys in terms of a common energy band (' d -band') to which both solute and solvent atoms contribute, and which is responsible for the magnetic properties. The variation of magnetic moment with composition is accounted for by a variation of the Fermi level as the electron concentration of the alloy is changed by altering the composition. This model seems to be oversimplified in a case where solute and solvent have atomic numbers differing by as much as do iron and palladium. Any refinement of the model seems to lead towards some characteristic localization of d -electrons, and hence of magnetic moment. There is good experimental evidence for such localization in binary alloys of pairs of elements both taken from

the first transition series, from observations on ferromagnetic disorder scattering and ferromagnetic superlattice scattering of neutrons (Shull and Wilkinson 1955).

Within the framework of this localized model, the simplest interpretation of a linear variation of alloy magnetic moment with composition is that it corresponds to a proportional combination of individual magnetic moments which do not each change with alloy composition. These individual moments are simply the respective extrapolations of the line to the 0% and 100% compositions. Adopting this procedure here, the straight part of fig. 4 may be extrapolated over that part of the phase diagram in which the face-centred cubic phase is unstable, to 100% of iron. A moment of 2.8 Bohr magnetons may thus be tentatively ascribed to each atom of iron in the face-centred cubic alloy. Some support for the procedure is given by applying it similarly to the face-centred cubic ferromagnetic phase in the following alloy systems; Ni-Fe, Co-Fe and Au-Fe. In each case the same moment is obtained, within the limits of experimental error.

Fig. 5



Estimated variation of moment per Pd atom, if the moment per iron atom remains about 2.8 Bohr magnetons at all compositions.

It thus seems reasonable to suggest that the iron moment in the Pd-Fe alloys may be about 2.8 Bohr magnetons, and not as great as its theoretical maximum of five. If this is the case, the moment per palladium atom for alloys with more than 10% of iron is of the order of 0.4 magnetons, and is roughly independent of composition. Of course, if the iron moment is actually lower than 2.8 units, the palladium moment must be correspondingly higher, but the main principles of this discussion remain unaffected.

In pure palladium ferromagnetism does not occur, nor has antiferromagnetism been found. Thus it seems that at $T=0$ the incompletely filled 4d band is unpolarized; there are equal numbers of electrons with either direction of spin. As iron is added to palladium in the range 0–10%, polarization of the palladium 4d band must therefore develop. A possible course of its development is shown in fig. 5, the form of which is based on an assumption of the moment on each iron atom remaining constant at 2.8 magnetons over this composition range. If the mean iron

moment tends to zero at zero concentration, of course, the palladium moment will rise more steeply than is shown in fig. 5, and become constant at a lower composition.

The explanation of the observed behaviour would seem to lie in two possible directions. Either on the one hand it is due to an intrinsic tendency towards ferromagnetism in pure palladium; the decrease in lattice parameter associated with alloying here permits Pd-Pd interactions to produce a ferromagnetic state: or on the other hand Pd-Fe interactions produce a resultant moment on the palladium atoms, and are primarily responsible for the ferromagnetic state. The present experiments do not appear to distinguish between these two cases.

The former possibility is that discussed by Wohlfarth (1956) in relation to the ferromagnetic behaviour of Ni-Pd alloys. That such small concentrations of iron produce ferromagnetism suggests that if this is the dominant mechanism, palladium is on the verge of being a ferromagnetic element. In this case, it is at first sight surprising that a non-magnetic solute such as copper, which also reduces the inter-atomic distance, produces no tendency towards ferromagnetism (Svensson 1932).

If the latter possibility is considered for the case of nearest-neighbour Pd-Fe interactions only, with no Pd-Pd interactions, it appears that ferromagnetic ordering throughout a disordered face-centred cubic crystal should occur if one of the twelve Pd atoms which are nearest neighbours to a given iron atom has another iron atom as a near neighbour. That is, there should be ferromagnetism down to compositions of the order of 2% of iron. For ferromagnetism to occur at much lower compositions, Pd-Pd interactions must also be present. This seems more likely to occur when those Pd atoms which are subjected to Pd-Fe interactions have a magnetic moment induced on them than otherwise.

Further work is in progress on more dilute Pd-Fe alloys.

ACKNOWLEDGMENTS

The author is grateful to Professor W. Sucksmith, F.R.S. for his interest and advice during the course of this work, and to the Mond Nickel Company for the loan of the pure palladium.

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Kinetics of Ordering in Fe_3Al [†]

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[Received November 12, 1959]

ABSTRACT

The resistance changes produced by thermal treatment of Fe_3Al have been measured and the annealing kinetics analysed. It was found that an increase in long-range order produced a large decrease in resistance. It was found that the rate at which ordering takes place is a function of the initial quenching temperature. All curves were fitted to the standard rate equation giving an order of reaction $n=2.2$ for specimens quenched from 620°C and $n=1.5$ for specimens quenched from 530°C . The activation energy obtained from resistivity kinetics was found to be much lower than the mean activation energy for diffusion.

§ 1. INTRODUCTION

IN the course of a series of experiments on the effect of ordering on the electrical resistivity of the alloy Fe_3Al , some data were obtained on the isothermal change of resistivity of an initially disordered alloy. The mathematical form of these isothermal annealing curves is to be analysed in the present paper.

The experiments were limited to two compositions both close to the stoichiometric alloy Fe_3Al . This alloy has a critical temperature of about 540°C . The characteristic (DO_3) superlattice disappears at this temperature, but according to recent data (Taylor and Jones 1958) an imperfect form of order of the CsCl (B2) type persists to above 700°C . This imperfect order has little effect on the physical properties; the alloy in this condition behaves almost as if it were disordered.

The only extant studies of ordering kinetics in Fe_3Al were carried out by Rode (1957) who measured resistivity and saturation magnetization, and by McQueen and Kuczynski (1959), who measured resistivity. However, none of these attempted any analysis of the form of his isothermal curves; this is the chief purpose of the present paper.

§ 2. EXPERIMENTAL PROCEDURE

Resistance specimens were formed from Fe_3Al alloys containing 24.8 at. % and 25.5 at. % aluminium. Purity of the constituents was better than 99.99%. Specimens were milled from $7\text{ cm} \times 1\text{ cm} \times 0.1\text{ cm}$ strips into the

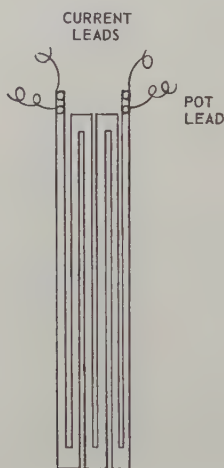
[†] Communicated by the Authors.

[‡] Now at Frankford Arsenal, Philadelphia, Pa.

form shown in fig. 1, giving an effective length of approximately 35 cm. By means of etchants the cross-sectional area of the specimens was reduced until the resistance reached a value between 0.1 and 0.2 ohms at 77°K. Current and potential leads were brazed to the specimens. Cold work was removed by vacuum annealing the specimens at 800°C for 4 hours.

The resistance measurements were made with a potentiometer by comparing the potential drop across the sample with the potential drop across a known resistance in series. Proper precautions against spurious thermal e.m.f.'s of thermoelectric origin were taken by the use of a reversing circuit. No attempts were made to obtain absolute values of the resistivity in view of the complex shape of the specimen. All resistance measurements were made at liquid nitrogen temperature.

Fig. 1



Shape of specimen used for resistivity studies.

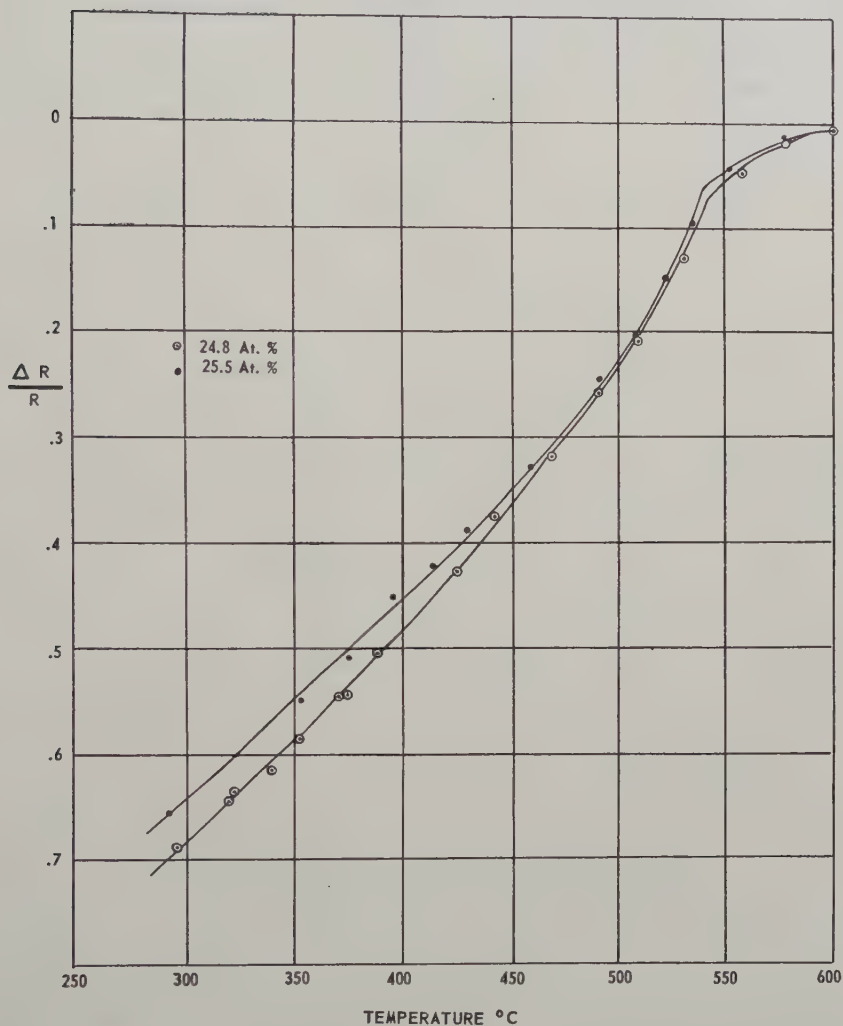
For the kinetic studies, specimens were brine quenched from 620°C and 530°C, temperatures respectively above and below the critical temperature (538°C). The brine quench was introduced to maintain the at-temperature state as efficiently as possible. The specimens were then inserted into a preheated slotted copper block inside the furnace in order to bring them quickly to the desired temperature of isothermal ordering. The specimen was withdrawn at intervals and quenched and the resistance was measured at 77°K before continuing the isothermal anneal. The kinetics of isothermal anneals were obtained for 295°C, 322°C, 353° and 375°C.

§ 3. EXPERIMENTAL RESULTS

Figure 2 shows the per cent change in resistivity (measured at 77°C) of 24.8 and 25.5% iron-aluminium as a function of the annealing temperature for infinite time. The data were so adjusted that a zero change refers

to the resistance of the specimen in the condition 'as quenched from $620^\circ C$ '. Each datum point represents the equilibrium value of the resistance for the temperature of its abscissa. Data points were obtained

Fig. 2



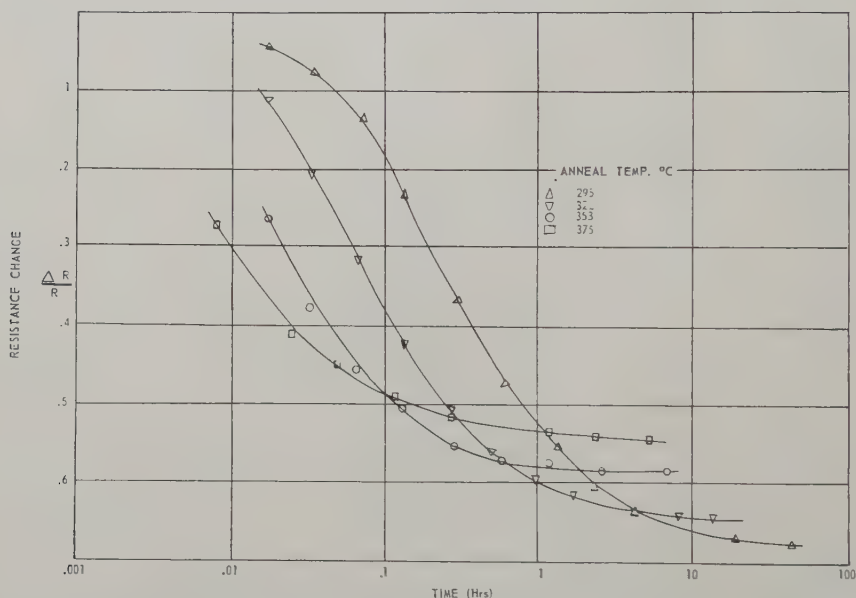
Equilibrium values of resistance. (All measurements made at $77^\circ K$.)

for temperatures above the critical temperature ($T_c = 538^\circ C$), where times to attain equilibrium were of the order of a few seconds, to temperatures well below T_c involving times of the order of 10 hours.

Isothermal data for the 24.8% aluminium alloy are shown in fig. 3 as a plot of the per cent changes in resistivity from an initial quench from $620^\circ C$. Similar data were obtained for 25.5% aluminium. Each value of

the change in resistance was measured at 77°C after the specimen was held at temperature for the time indicated and then brine quenched. It should be noted that as the temperature of anneal is increased the initial slope, related to the rate of reaction, has also increased. The equilibrium resistance for higher temperatures is reached in a shorter period of time but the total resistance change is smaller, thus giving rise to a 'cross over' effect, i.e. the higher the temperature the greater is the equilibrium resistance. The final values of these curves are plotted in fig. 2 and the curves of fig. 3 indicate the method used to determine the time necessary to attain equilibrium.

Fig. 3



Isotherms of resistance change vs. annealing time for 24.8 at. % alloy specimens. Initially quenched from 620°C and measured at 77°K.

Similarly, isothermal annealing curves were obtained for specimens quenched from just below the critical temperature ($T_g = 530^\circ\text{C}$) after 10 hours of soaking at temperature. Again only the results for the 24.8% aluminium alloy are shown in fig. 4. The data were adjusted so that the ordinate origin corresponds to the resistance for the 620°C quench. This may be done by utilizing $\Delta R/R$ for a change in temperature from 620°C to 530°C from fig. 2.

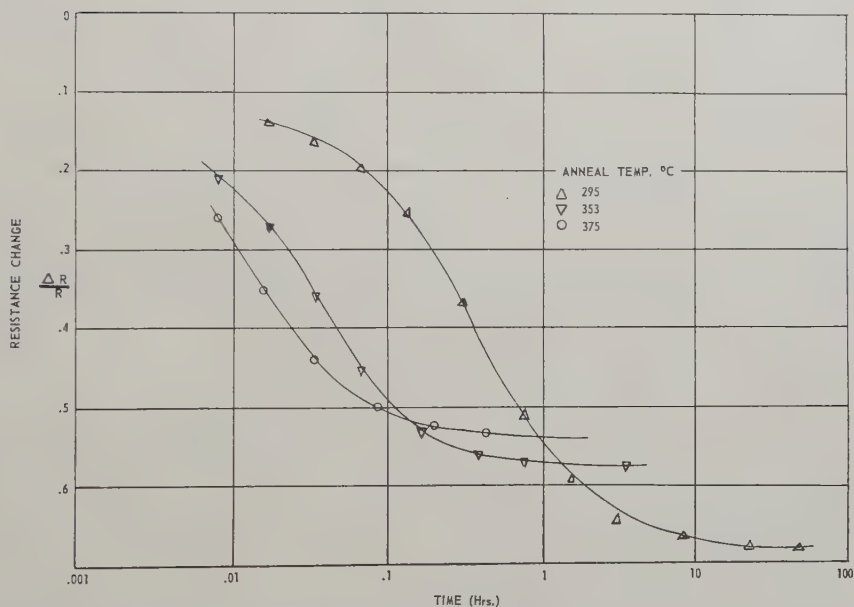
The isothermal annealing curves were analysed by standard techniques based on integrated rate equations for the order of reaction n . n is defined by the following standard differential equation.

$$\frac{d\rho}{dt} = -\frac{1}{\tau_n} (\rho_t - \rho_\infty)^n \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $d\rho/dt$ is the rate of change of resistivity, τ_n is the rate constant, ρ_t is the resistivity at time t and ρ_∞ is the resistivity for infinite time. A high order of reaction is characterized by a reaction rate which decreases rapidly with increasing time. According to Parkens *et al.* (1951) solid state rate processes are normally regarded as being of first order. From this point of view, the experimental curves which are characterized by higher order ($n > 1$) indicate that a distribution of activation energies is involved. Activation energies are obtained from the rate constant τ , which can be represented by an Arrhenius equation

$$\tau = \tau_0 \exp(H/KT).$$

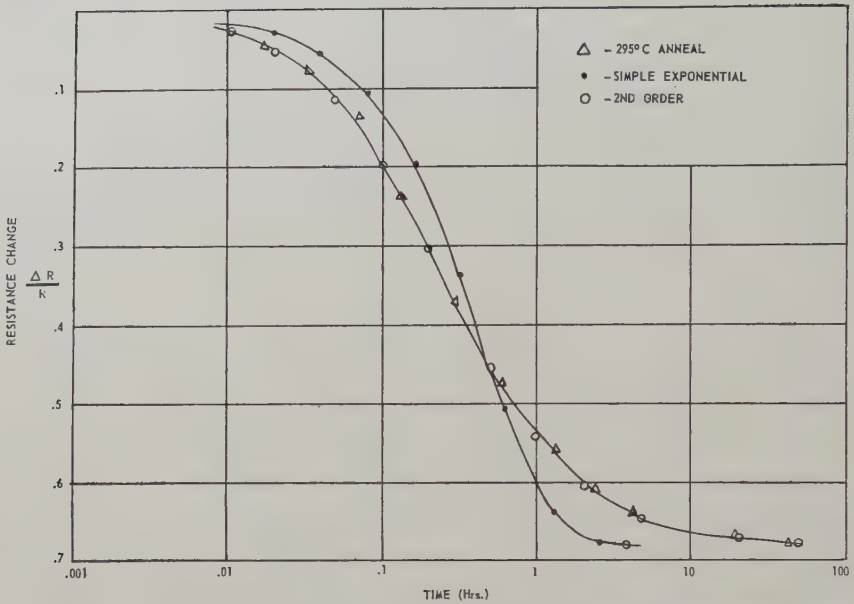
Fig. 4



Isotherms of resistance change vs. annealing time for 24.8 at. % alloy. Specimens initially quenched from 530°C and measured at 77°K.

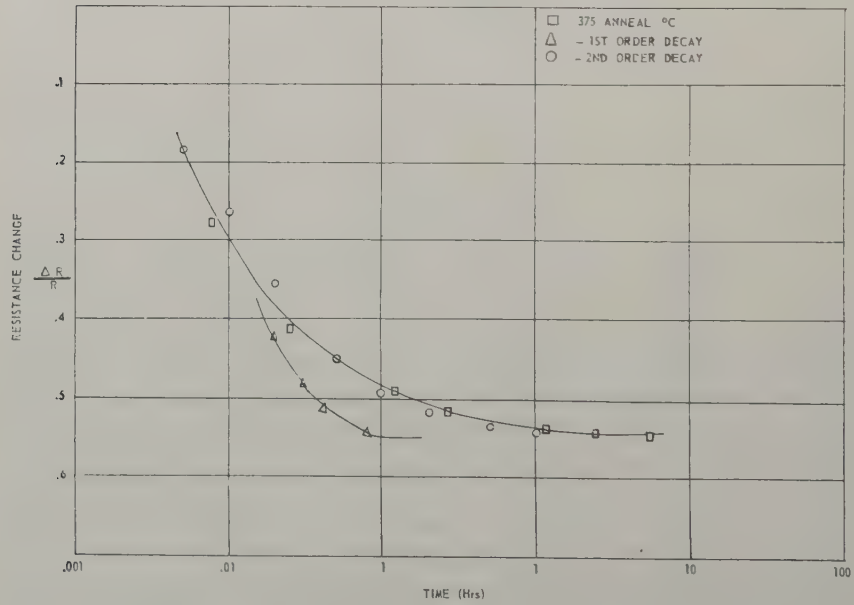
The triangles in fig. 5 show a typical isothermal (295°C) anneal curve of the 24.8% aluminium alloy quenched from 620°C. One of the lines represents a first order decay curve of the form $d\rho/dt = -(1/\tau)(\rho_t - \rho_\infty)$. Integration of this equation leads to the identification of a relaxation time τ_1 , as the time required to achieve all but $1/e$ of the total change in the resistance at any given temperature. Each computed curve has been fitted to the experimental curve at $t=0$, $t=\tau_1$ or τ_2 and $t=\infty$. (The relaxation time τ_2 corresponding to the second order equation is derived in the way explained in the Appendix.) It is seen that the first-order curve does not fit the data very closely. A mathematical second-order curve, represented by the open circles, makes a very good fit over the entire experimental curve.

Fig. 5



Comparison of first- and second-order curves for a 295°C isothermal anneal. 24.8% specimen, initially quenched from 620°C.

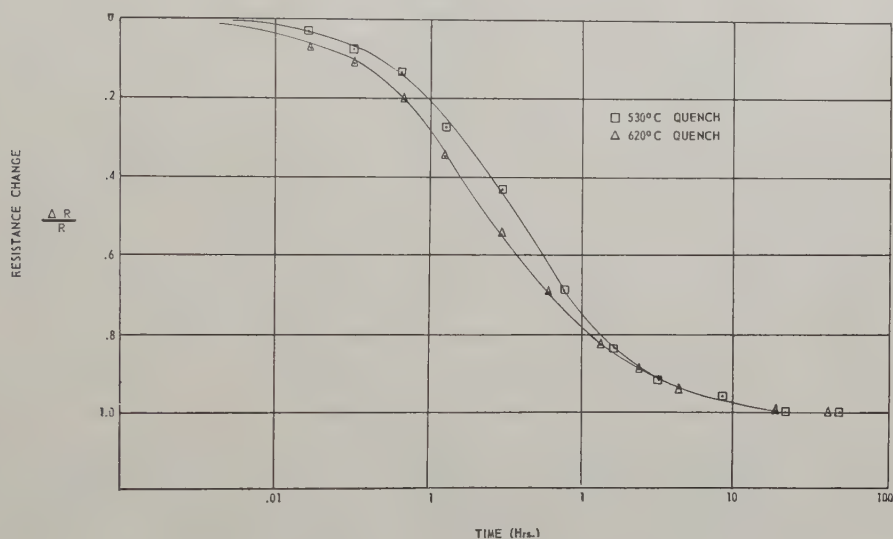
Fig. 6



Comparison of first- and second-order curves for a 375°C isothermal anneal. 24.8% specimen, initially quenched from 620°C.

For comparison purposes, mathematical first-order and second-order curves were plotted and compared with a 375°C anneal curve as shown in fig. 6. The second-order curve indicates a good fit for times greater than τ and a poor fit for the times less than τ . On the other hand, the second-order curve as fitted to the 295°C anneal (in fig. 5) indicates a good fit throughout the entire curve. A more exact determination of the reaction order from the experimental data was obtained by means of a graphical method (Chang 1957) and also by an analytical method (Rothwarf and Steinberg 1959, private communication). The average order of reaction was 2.2 (i.e. the value of n in the formulae given in the Appendix is 2.2). Similar analyses made on specimens quenched from 530°C, below the critical temperature (fig. 4), gave 1.5 for the order of reaction. The difference in

Fig. 7



Normalized 295°C isotherms measured at 77°K.

ordering rates can be seen very clearly in fig. 7, which is a plot of the 295°C isothermals (normalized at $t=0$ and $t=\infty$) indicating an increase in the rate of ordering with an increase in quenching temperature. This is to be expected for reaction orders greater than unity. Figure 8 shows a plot of the relaxation time τ as a function of the reciprocal temperature for all isothermal curves measured in these experiments. The upper plot gives the activation energy for specimens quenched from 530°C and the lower plot gives the activation energy for specimens quenched from 620°C. The two plots were obtained from the original isothermals by assuming an order of reaction of 1.5 and 2.0 respectively†. The activation energy is obtained from the slopes of the straight lines. Since each set of points lies

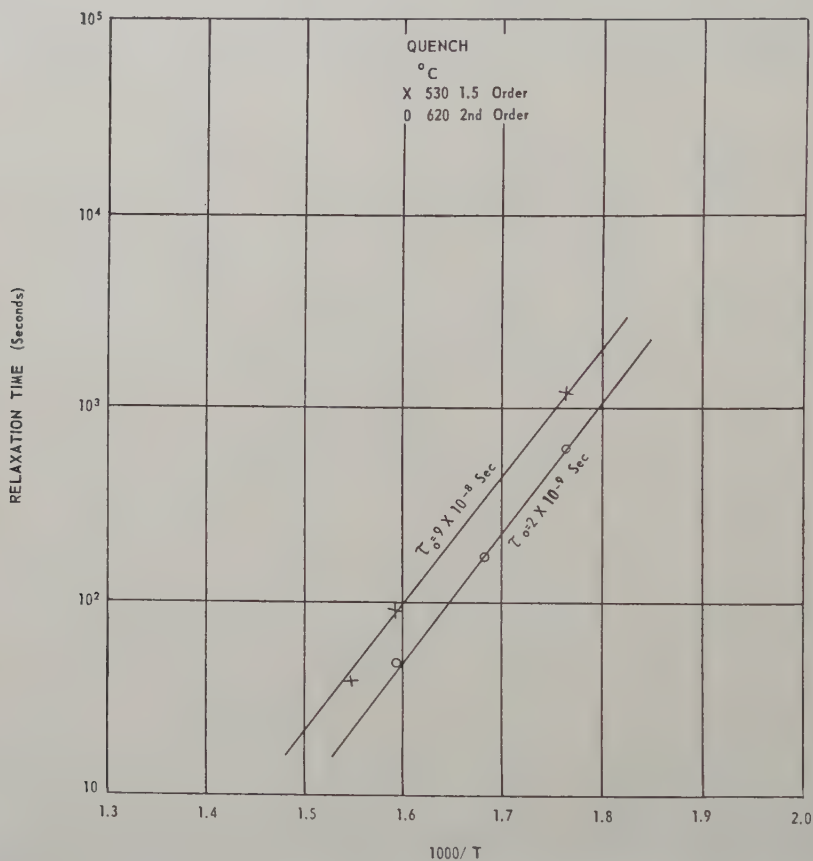
† τ_0 , the value of τ for $1/T=0$, is also shown in the figure.

on a straight line and the lines are reasonably parallel, one can infer that the rate of annealing is determined by a single activation process over the temperature range investigated.

§ 4. DISCUSSION

The results summarized in the previous section indicate that, in the 24.8 at. % Fe/Al alloy, the rate at which ordering takes place is a function of the initial quenching temperature. In the table, (A) gives the values of the

Fig. 8



Variation of relaxation time with reciprocal absolute temperature for a 24.8 at. % Fe/Al alloy.

order of reaction as a function of annealing temperature for different quenches; (B) gives similar results for the specimens of 25.5 at. % Fe/Al treated in the same fashion. Except for one 295°C annealed specimen in (B) there is a strong correspondence of order of reaction with quenching temperature. Within experimental error there is no correlation of n with annealing temperature.

By way of example, the 295°C anneal for both quenches (24.8 at. % alloy) was normalized and plotted as a function of time (see fig. 7). The specimen quenched from the higher temperature is seen to have a faster initial ordering (indicative of a higher order of reaction) prior to the inflection point and a slowly decreasing rate of approach to equilibrium. This is similar to the experimental results reported by Brinkman *et al.* (1954) for Cu_3Au , and by Kuczynski *et al.* (1955) for $CuAu$. It is possible that the initial increase in rate of ordering should be attributed to an increase in the density of quenched-in vacancies. The result of this however would be that the process was no longer singly activated; i.e. no single value of n would be adequate for the entire curve. This is contrary to our findings.

(A) (24.8%)		
Anneal °C	n , quench 620°C	n , quench 530°C
295	2.25	1.6
322	2.20	
353	2.25	1.4
375	2.3	1.6
(B) (25.5%)		
295	2.3	1.95
353	2.3	1.4
375	2.5	1.4
383		1.5

The initial states should of course be influenced by the differences in atomic arrangement which exist at different quenching temperatures. For ordering temperatures well below T_c , however, nucleation is not rate-determining (see for instance Burns and Quimby 1955), and the growth rate of ordered regions will depend on the free energy difference between the initial and final states. This will be the greater, the higher the temperature from which the alloy is quenched.

The fact that a well-defined single activation energy is obtained by the present method is no doubt due to the narrowness of the range of temperatures investigated. According to Burns and Quimby's (1955) resistivity kinetic data for Cu_3Au , as interpreted by Vineyard (1956), a plot such as that in fig. 8 should give curved lines whose slopes diminish as T approaches T_c . However, the curve approximates to a straight line at low temperatures. According to Vineyard's theory, if the temperature range is one in which the equilibrium degree of order is almost constant, then the deduced activation energy for ordering should be the mean of the activation energies for self-diffusion of the two components in the alloy.

The values of the rate constant plotted in fig. 8 give a well-defined activation energy of 31 kcal/mole. Similar results were obtained for the 25.5 at. % alloy. This is to be compared with a value of 29.5 kcal/mole reported by Rode (1957). It is known that self-diffusion in pure iron has an activation energy of about 73 kcal/mole (Birchenall and Mehl 1950). The mean activation energy for diffusion of aluminium in iron is 57.3–58.6 kcal/mole (Gröbner 1955, Shyne 1958). The apparent activation energy obtained for Fe_3Al is, therefore, a good deal lower than that for any diffusion process (unless indeed the activation energies for solute and self-diffusion are sharp functions of composition or of the state of order, which cannot be entirely excluded). However, this disparity is not really surprising, since the degree of order is still changing appreciably with temperature in the range 295°C–375°C. A comparison with the corresponding data for Cu_3Au (cf. fig. 4 in Vineyard's paper) shows that in this case also the apparent activation energy deduced from resistivity kinetics is much lower than the mean activation energy for diffusion, in a temperature range in which the rate of change of degree of order with temperature is variable. What is rather surprising is the fact that the plots in fig. 8 of the present paper are such good straight lines; on the basis of Vineyard's theory these plots would be expected to be considerably curved. In spite of the fact that a well-defined activation energy is found from fig. 8, it appears probable that this has no real physical significance.

ACKNOWLEDGMENTS

We are grateful to Professor G. V. Raynor for his support, and the provision of laboratory facilities. One of us (R. F.) is indebted to the Secretary of the U.S. Army for a Fellowship.

APPENDIX

The general n th order rate equation is

$$\frac{d\rho}{dt} = -\frac{1}{\tau_n}(\rho_t - \rho_\infty)^n. \quad (1)$$

Integration of this leads to the following equation:

$$(\rho_t - \rho_\infty)^{-(n-1)} = \frac{(n-1)t}{\tau_n} + (\rho_0 - \rho_\infty)^{-(n-1)} \quad (2)$$

where ρ_0 = initial resistance, ρ_∞ = resistance at infinite time, ρ_t = resistance at any time t .

Equation (2) is equivalent to

$$(\rho_t - \rho_\infty) = \left[\frac{(n-1)t}{\tau_n} + (\rho_0 - \rho_\infty)^{-(n-1)} \right]^{-1/(n-1)}.$$

Solving for ρ_t , one obtains

$$\rho_t = \rho_\infty + (\rho_0 - \rho_\infty) \left[\frac{(n-1)(\rho_0 - \rho_\infty)^{n-1}t}{\tau_n} + 1 \right]^{-1/(n-1)}. \quad (3)$$

For the special case of a first order equation ($n = 1$), equation (3) becomes

$$\rho_t = \rho_\infty + (\rho_0 - \rho_\infty) \exp(-t/\tau_1). \quad (4)$$

Theoretical curves were, as a matter of convenience, always fitted to experimental data at $t = 0$, $t = \infty$, and a time t' at which all but $1/e$ of the total resistance change has been completed. For a first-order reaction, $t' = \tau_1$. Using this fact, one can calculate the relaxation time τ_n for any desired order of reaction, as fitted to the experimental data :

Values of ρ_t , computed from eqns. (3) and (4), are set equal. We then have

$$\exp(t/\tau_1) = \left[\frac{(n-1)(\rho_0 - \rho_\infty)^{n-1}t}{\tau_n} + 1 \right]^{1/(n-1)} \quad (5)$$

and solving this for τ_n ,

$$\tau_n = \frac{(n-1)(\rho_0 - \rho_\infty)^{n-1}t}{\exp\{(n-1)t/\tau_1\} - 1}. \quad (6)$$

Curve fitting is carried out at $t = t'$, and this value of t must therefore be substituted into eqns. (5) and (6). Since $t' = \tau_1$, we finally obtain

$$\tau_n = \frac{t'(n-1)(\rho_0 - \rho_\infty)^{(n-1)}}{\exp(n-1) - 1}. \quad (7)$$

t' is known from curve-fitting, and thus τ_n can be calculated from eqn. (7). Using this value of τ_n in eqn. (3), the computed n th order curve can be compared with the data points; this is done for various values of n until a good fit is obtained throughout. (If this proves possible for some one value of n , then the reaction is a 'singly activated' one). A fit may be obtained for a non-integral value of n . It appears reasonable to ascribe such a non-integral order of reaction to a single step process. This assumption is made since it is not possible to derive an expression of the form of eqn. (3) for the sum of several independent processes each characterized by an integral value of n . In view of this, only two physical interpretations remain for a reaction of non-integral order. Either the reaction is in fact occurring as a single-step process, or some type of coupling exists between two or more distinct processes.

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The Refractive Indices of Liquid and Solid Argon†

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[Received January 27, 1960]

ABSTRACT

The refractive indices of liquid and solid argon have been measured as a function of temperature between 74° and 95°K. The results, represented by the Lorentz-Lorenz function, are expressed as a function of density, and their significance discussed.

THE theory of dielectric materials, based on the Lorentz local field model, predicts that for a non-polar material the Clausius-Mossotti function $(\epsilon - 1)/(\epsilon + 2)\rho$, or its equivalent, the Lorentz-Lorenz function

$$(n^2 - 1)/(n^2 + 2)\rho,$$

should be independent of density (ρ). Measurements at low densities on the compressed gases argon (see for example Michels and Botzen 1949, Michels *et al.* 1951) and carbon dioxide (Michels and Kleerekoper 1939) show that although these functions are indeed nearly independent of density, they increase slowly with increasing density up to 2-300 Amagats and decrease at higher density. Measurements on liquids such as benzene (see for example Gibson and Kincaid 1938) suggest that the decrease is continued at higher density. The specific influence of temperature is very small.

In view of the crude nature of the model, and the over-simplification involved in assigning a polarizability to each atom, better agreement over such a wide range of density would hardly be expected. However, modifications to the theory, such as that of Jansen (1958), who analysed the effect of pair interactions upon the polarizability, or of ten Seldam and de Groot (1952), who considered the effect of compression on the atomic polarizability, can be made to account for slow variations of these functions.

In order to provide suitable data for the development of a more exact theory we have measured the refractive index of liquid argon (from 84-95°K) and more particularly of solid argon (from 74-84°K) in equilibrium with vapour. No accurate data appear to exist for non-polar

† Communicated by the Authors.

Fig. 1

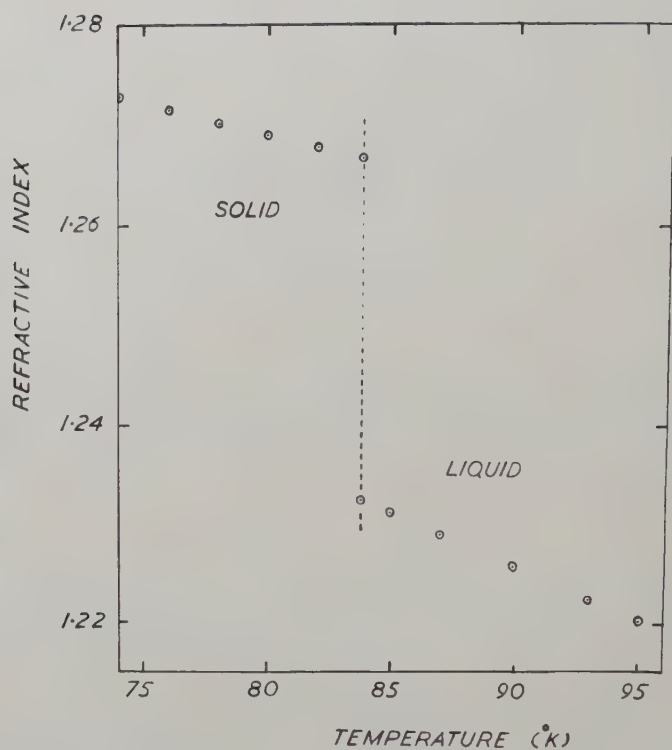
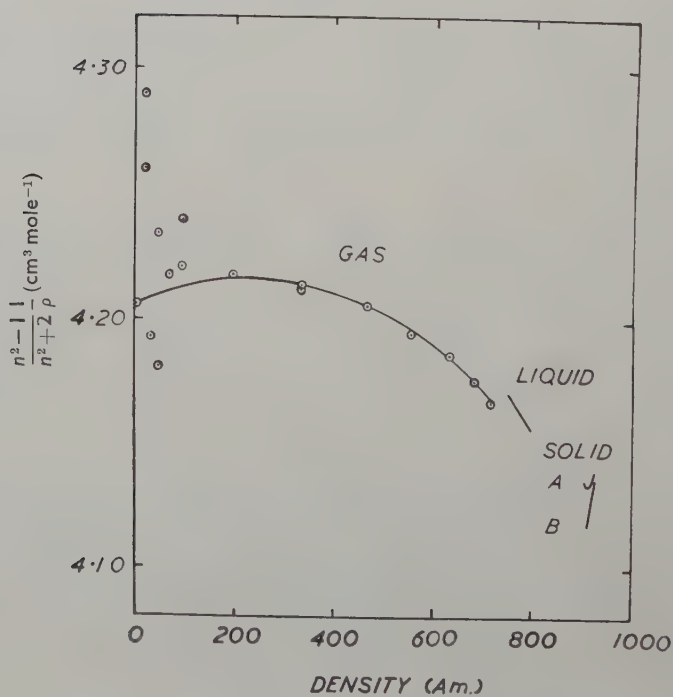


Fig. 2



solids and argon is especially suitable because of the nature of the inter-atomic force, which more nearly justifies the use of an atomic polarizability and which, being spherically symmetrical, offers better hope of an accurate treatment of pair interactions. Also, solid argon has the cubic symmetry of the Lorentz model.

The spectrometric method of minimum deviation was employed. The specimen was condensed into a hollow Perspex prism contained in a simple cryostat and located at the axis of rotation of a spectrometer mounted outside the cryostat on a co-axial turntable. Measurements were made at several wavelengths and those at $5893 \text{ \AA}$ are shown in fig. 1. At the triple point (83.8°K) the refractive index of the solid is 1.2670 ± 0.0005 and of the liquid 1.2330 ± 0.0005 . Since the nearest absorption band is in the ultra-violet, dispersion is small.

In fig. 2 the Lorentz-Lorenz function is plotted against density for the data of fig. 1 and for those of Michels and Botzen at $5876 \text{ \AA}$. For our computations the density of the liquid (ρ_L) was taken from the data of Piercey (1957) and of Mathias *et al.* (1912), and the density of the solid (ρ_S) from the results of Dobbs *et al.* (1956). In the results of these authors as plotted, the experimental curve for solid argon was drawn through the point corresponding to the value ($1.621 \text{ g c.c.}^{-1}$) quoted by Clusius and Weigand (1940) at the triple point. However, the recent measurements of ρ_L by Piercey indicate that the extrapolated value for ρ_L at the triple point from which Clusius and Weigand derived their estimate of ρ_S was too low. We have therefore drawn two curves to represent the behaviour of the solid. Curve A makes use of the values of density obtained from the published curve of Dobbs *et al.* and curve B of values obtained by attaching slightly more weight to their results and re-drawing their curve to a higher value ($1.6275 \text{ g c.c.}^{-1}$) at the triple point. The differences between these two curves then illustrate the limiting interpretations which can reasonably be given to the results for refractive index.

It will be seen that for liquid argon the Lorentz-Lorenz function decreases by about 0.3% over the range of densities studied, roughly as would be expected from the behaviour of the gas at lower densities. For solid argon the results appear to indicate an increase with increasing density, at least at the higher densities, and point to the desirability of obtaining still more accurate values of the density near the triple point. At present no appropriate theoretical treatment exists by which the effect of pair interactions upon the polarizability at large amplitudes of vibration may be evaluated.

ACKNOWLEDGMENTS

We are grateful to Dr. E. R. Dobbs for helpful discussions and to the D.S.I.R. for a research studentship awarded to one of us.

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Isotopic Spin Selection Rules

XIII: The 6.92 MeV State of ^{16}O Revisited†

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[Received January 16, 1960]

ABSTRACT

The status of the possible E1-E3 cascade between the $2+$ state at 6.92 mev, the $3-$ state at 6.14 mev and the $0+$ ground state of ^{16}O is reviewed in the light of recent improvements in our knowledge of radiative transitions and isotopic spin impurities. It is concluded that the present limit of 5×10^{-3} on the relative intensity, although clearly demonstrating the efficacy of the isotopic spin selection rule, is not sharp enough to be a significant test for detailed models of the nuclear structure, for which purpose an improvement by an order of magnitude would be required. It is shown by a coincidence method, using the reaction $^{19}\text{F}(p, \alpha)^{16}\text{O}$, that the relative intensity is less than 4×10^{-4} . This corresponds to $\alpha_0^2(1) < 2 \times 10^{-3}$, a low figure.

§ 1. INTRODUCTION

THE first paper of this series (Wilkinson and Jones 1953) pointed out that the E1 transition between the $2+$ state of ^{16}O at 6.92 mev and the $3-$ state at 6.14 mev is subject to the isotopic spin selection rule forbidding E1 transitions of $\Delta T = 0$ in nuclei of $T_z = 0$. Consequently what might have been expected as favourable competition with the E2 transition to the ground state is strongly inhibited: the experimental result of that paper was that the E1 transition is no more than 5×10^{-3} of the E2. Since that time our understanding both of the most probable speeds for uninhibited E1 transitions in the light nuclei (Wilkinson 1958) and also of the empirical and theoretical behaviour of isotopic spin impurity (MacDonald 1956, Wilkinson 1958) has greatly increased. The situation relative to ^{16}O was summarized some time ago (Wilkinson 1956). From this summary it appeared that the 1953 experimental limit on the E1 versus E2 branching ratio although clearly demonstrating the T -forbiddenness was not sharp enough to test our later and more detailed ideas about isotopic spin purity since it implied that $\alpha_0^2(1)$ (the intensity of the $T = 1$ impurity) is less than a few per cent whereas the expectation for $\alpha_0^2(1)$ at that excitation is 10^{-3} to 10^{-2} . Since 1956 the

† Communicated by the Authors. Work performed under the auspices of the United States Atomic Energy Commission.

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situation has been made quite definite by the measurement of the mean lifetime of the 6.92 mev state as $(1.2 \pm 0.3) \times 10^{-14}$ sec (Swann and Metzger 1957). This enables us to interpret the branching ratio in terms of an actual rather than an estimated lifetime; no sensible change was introduced into the earlier analysis.

If we use the systematics (Wilkinson 1958) to estimate the most likely mean lifetime for an 0.78 mev uninhibited E1 transition in ^{16}O we find about 6.6×10^{-14} sec. So were the E1 unaffected by the isotopic spin rule we should expect its strength relative to the E2 to be about 0.18. The old limit of 5×10^{-3} therefore corresponds, using the newer data and systematics, to $\alpha_0^2(1) < 0.028$ (with the inevitable uncertainty introduced by guessing the speed of the uninhibited E1 transition mixed in through the isotopic spin impurities). It is therefore clear that an improvement by an order of magnitude in sensitivity to the E1 branch would be very interesting and would bring us to the point where the cascade should probably show up unless it is in fact further inhibited by something peculiar to the ^{16}O structure and having nothing to do with isotopic spin. We do not expect this for the following reason. The E2 transition is strong ($|M|^2 \simeq 0.7$) and so must contain strong components differing from the (closed shell) ground state of ^{16}O by a single particle: $1p^{-1}(2p, 1f)$ and $1s^{-1}1d$. The 3- state is well contained by the independent particle treatment of Elliott and Flowers (1957) which describes it as $1p^{-1}1d$. The Coulomb perturbation will mix in the $T=1$ parts of these same configurations (cf. the explicit treatment of the 1- state at 7.12 mev made by Elliott and Flowers) and so it is difficult to see how the E1 transition can be additionally inhibited on grounds of nuclear structure since the descriptions of the two states given above differ in all components by one-particle one-quantum jumps of the equivalent oscillator. An additional important component in the isotopic spin impurity of well-spaced states is thought to come from the Coulomb mixing of one-particle two-quantum excitations of the type $(n, j) \rightarrow (n+1, j)$ (MacDonald 1956). If we apply this recipe to generate $T=1$ impurities for the two states in question we find:

$$2+ (T=0): 1p^{-1}(2p, 1f) + 1s^{-1}1d;$$

$$3- (T=1): 1s^{-1}1p^{-1}2s1d + 1p^{-2}1d2p;$$

and

$$2+ (T=1): 1s^{-1}1p^{-1}2s(2p, 1f) + 1p^{-2}2p(2p, 1f) + 1s^{-2}2s1d + 1s^{-1}1p^{-1}1d2p;$$

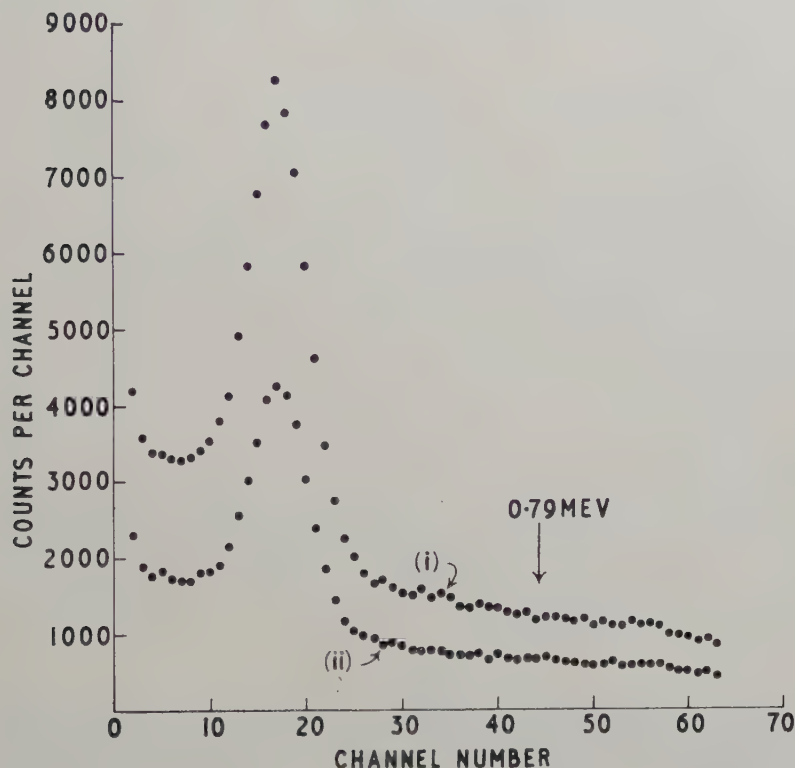
$$3- (T=0): 1p^{-1}1d.$$

The $2+ (T=1) \rightarrow 3- (T=0)$ transitions are forbidden but the $2+ (T=0) \rightarrow 3- (T=1)$ are allowed unless the $2+$ state is entirely $1p^{-1}1f$. This last possibility can be discounted since interaction between configurations is clearly needed to produce the large downward energy displacement implied by this state of two-quantum excitation appearing at so low an energy as 7 mev. We therefore have no reason to anticipate a strong additional inhibition of the E1 transition and it becomes interesting to press the matter further.

§ 2. EXPERIMENT

The 6.92 mev $2+$ ^{16}O state was populated by using the resonance in $^{19}\text{F}(p, \alpha)^{16}\text{O}$ at a proton energy of about 2.4 mev. The target of BaF_2 was about 50 kev thick. At this resonance the 6.92 mev state is fed about three times more strongly than the $1-$ state at 7.12 mev while the feeding of the 6.14 mev $3-$ state is relatively weak (Swann and Metzger 1957). Coincidences between the 0.78 mev E1 transition and the 6.14 mev E3 to the ground state were sought using a coincidence resolving time of about 0.1 μsec .

Fig. 1

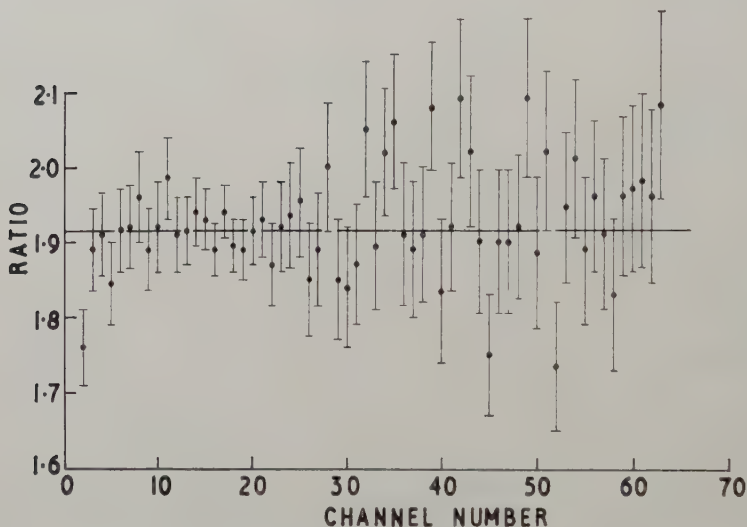


Low energy spectrum seen in coincidence with (i) the 5.4–6.5 mev bracket in the high-energy crystal; (ii) the 6.7–7.7 mev bracket. The peaks at channel 17 are due to annihilation radiation; the arrow indicates the expected position of the 0.78 mev line which might show in curve (i) but not in curve (ii).

The high energy gamma-rays were detected in a 5 in. $\times$ 5 in. cylindrical NaI(Tl) crystal placed at 80° to the proton beam. The gamma-rays were collimated by a hole in the form of a truncated cone of height $2\frac{1}{2}$ in. base diameter $1\frac{3}{4}$ in. and entrance diameter $\frac{1}{2}$ in. through a lead shield. The entrance was 7/16 in. from the centre of the BaF_2 target. The low energy

gamma-ray was sought in a 3 in. $\times$ 3 in. cylindrical NaI(Tl) crystal placed 'out of sight' of the irradiated face of the larger crystal. The smaller crystal was $1\frac{11}{16}$ in. from the centre of the target and was placed at about 45° to the proton beam on the side away from the larger crystal. This arrangement was adopted to minimize coincidences due to scattering between the crystals and to the detection of annihilation radiation following pair conversion in the larger crystal. The smaller crystal was that used in the research on cascade de-excitation in ^{13}C (No. XIV of this series) and had a resolution of 7.6% for gamma-rays of 0.78 mev (see fig. 3 of paper XIV).

Fig. 2



The ratio channel by channel of the counts in spectra (i) and (ii) of fig. 1.

The coincidences between the two crystals were displayed on a 32×64 channel kicksorter made at Brookhaven National Laboratory under the direction of Mr. R. Chase. The 32 channel axis displayed the pulses in the larger crystal between energies of approximately 4 and 8 mev; the energy range of the smaller crystal's display along the 64 channel axis was approximately 0.35 to 1.0 mev. For purposes of display and discussion here we present severally in fig. 1 the low-energy spectra summed between channels 15-23 and between channels 24-31 of the high energy arm. The lower range corresponds to the energy spread 5.4-6.5 mev in the larger crystal and the upper corresponds to 6.7-7.7 mev. If the E1-E3 cascade is present the 0.78 mev line will be seen in coincidence with the 5.4-6.5 mev range of the larger crystal but will not be seen in coincidence with the 6.7-7.7 mev bracket.

It is clear from fig. 1 that no strong 0.78 mev line is present. The peak seen at channel 17 in both spectra is due to annihilation radiation. The form of the two low-energy spectra in coincidence with the two high energy brackets are effectively identical as is seen in fig. 2 where their ratio is displayed. This suggests a method of analysis that does not depend on assumptions about the form of the background underlying the possible 0.78 mev peak. We consider the channel range 40-49 that straddles the position expected for the 0.78 mev peak. From the total number of counts in this range of the spectrum in coincidence with the 5.4-6.5 mev bracket we subtract the corresponding total number taken from the spectrum in coincidence with the 6.7-7.7 mev bracket multiplied by the mean ratio for the entire spectra derived from the data presented in fig. 2. The difference so derived is 87 ± 190 counts.

An alternative though not so direct treatment of the data is to analyse that portion of pulse spectrum (i) of fig. 1 that excludes the peak region in polynomial form and then use this analysis to predict the number of counts expected for the peak region in the absence of a peak. This has been done by Dr. P. E. Hodgson of the Clarendon Laboratory, Oxford to whom our best thanks are due. Channels 28-39 and 50-63 were used to derive a best polynomial fit (4th order). This polynomial fit thus predicts 12204 ± 72 counts for the peak region of channels 40-49. The observed number is 12250. The difference of 46 ± 132 counts is to be compared with the 87 ± 190 of the direct method. We say that the difference is zero within a standard deviation of 190 counts, preferring to use the indirect solution as strong confirmation of the direct method.

Both crystals were carefully calibrated for their response to a range of monochromatic gamma-rays so that their efficiencies within the various energy ranges of interest were known. By these means we can say that the E1-E3 branch relative to the E2 transition to ground from the 6.92 mev state is zero within a standard deviation of 2.3×10^{-4} .

§ 3. DISCUSSION

It appears that the branching ratio is most probably less than 4×10^{-4} . This, following the considerations of § 1, corresponds to a probable upper limit on the isotopic spin impurity by intensity of about 2×10^{-3} . This figure is quite low in the expected range $10^{-3} < \alpha^2 < 10^{-2}$ though not so low as to be disturbing in view of the possible vagaries of the many matrix elements involved in the comparison with a very approximate theoretical model. It is, however, low enough to be interesting and to be a useful test of detailed attempts to describe the $2+$ state. So far no thorough-going theoretical comparison is available for this transition as it is for the forbidden E1 transition to ground from the $1-$ state at 7.12 mev which has $\alpha_0^2(1) \simeq 7 \times 10^{-3}$ expressed under our present conventions outlined in § 1 (Wilkinson 1958) and which is well described by the independent particle model (Elliott and Flowers 1957).

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Isotopic Spin Selection Rules

XIV: Transitions between Mirror States in ^{13}C and $^{13}\text{N}^\dagger$ By J. V. KANE, R. E. PIXLEY and D. H. WILKINSON ‡

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[Received January 16, 1960]

ABSTRACT

The 3.68 mev $3/2^-$ state of ^{13}C is shown, by a coincidence technique to cascade via the 3.09 mev $1/2^+$ state with a probability of $(6.5 \pm 1.0) \times 10^{-3}$. The rule that corresponding E1 transitions in mirror nuclei have the same reduced speed, i.e. are mirror transitions, is used to deduce the speed of this weak branch from data available in ^{13}N and hence to determine the radiative width of the M1 transition to ground from the 3.68 mev state. This is (0.40–0.75) ev. The speed of this transition, which is not a mirror transition to the corresponding one in ^{13}N , is compared with the prediction of the independent particle model. Agreement is obtained within the range of the intermediate coupling parameter a/K that satisfies other data in the $A=13$ system.

§ 1. INTRODUCTION

THE close comparison between the energies of excitation of corresponding states in mirror nuclei is due to the charge independence or charge symmetry of the specifically nuclear part of the nucleon–nucleon interaction. The charge-dependent Coulomb energy is considerable and produces a gross mass difference of several million electron volts between the members of the isobaric multiplet; it does not, however, affect the comparison between the level structures of the several T_z nuclei since it is, to a good first approximation, independent of the energy of excitation at least when that energy is low. Because of this one often tends to lose sight of the very real differences between mirror nuclei for those phenomena that are essentially charge-dependent in character. In particular we have no *a priori* reason to expect that the reduced speed of the electromagnetic transition between a given pair of states in a given nucleus will be unchanged for the corresponding transition between the mirror states in the mirror nucleus. The states are mirror states but the corresponding transitions are not in general mirror transitions.

† Communicated by the Authors. Work performed under the auspices of the United States Atomic Energy Commission.

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There are several classes of exception to this general expectation that the reduced speed will depend on T_z and they have been discussed by Morpurgo (1959). The one of interest to us here is that the reduced speed is independent of T_z for E1 transitions. This rule is closely connected with the familiar isotopic spin selection rule on E1 transitions and may be easily understood by considering the Hamiltonian H of the electromagnetic interaction as split up in the usual way :

$$H = H_0 + H_1.$$

For $\Delta T = 0$, M_1 is proportional to T_z ; for $\Delta T = \pm 1$ M_1 depends on T_z^2 . In general, then, corresponding transitions between states with $\Delta T = \pm 1$ have the same reduced speed in the mirror nucleus, i.e. are mirror transitions, since then $M_0 = 0$, but for $\Delta T = 0$ the corresponding transitions have different reduced speeds since generally both M_0 and M_1 contribute. For E1 transitions, however, M_0 makes no contribution owing to conservation of total momentum (cf. the derivation of the E1 isotopic spin selection rule—e.g. MacDonald 1955) and so the reduced E1 speed is the same in both members of the mirror pair†.

Accordingly we can in general make no model-independent remark about the relative speeds of the corresponding transitions in the members of a mirror pair although Morpurgo (1959) has given reasons why we should not expect the speeds of corresponding M1 transitions to be greatly different in reasonable circumstances.

This situation is to be welcomed since it gives added opportunity for the testing of nuclear models which must be required to account for the differences between mirror nuclei as well as their similarities.

At present there exist almost no data on the comparison of corresponding but non-mirror transitions (e.g. M1) in nuclei for which a detailed model exists to be tested by the results. It is the purpose of this paper to provide one such comparison in a case which has received extensive theoretical treatment.

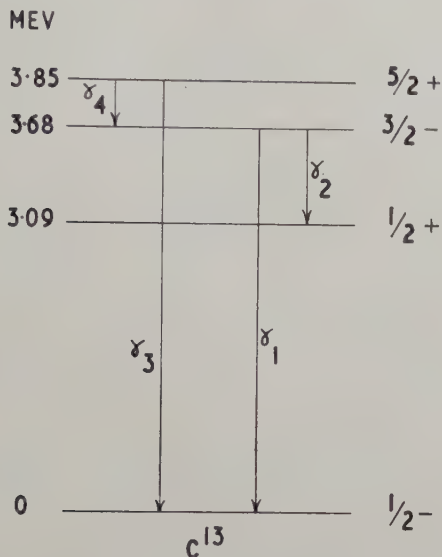
§ 2. STATES OF ^{13}C AND ^{13}N

The low-lying odd-parity states of $A = 13$ made from p^9 have been extensively treated on the independent particle model (IPM)—Inglis (1953), Kurath (1956), Lane (1953, 1955). Lane in particular has emphasized that a substantial group of experimental data is unified within the IPM by receiving satisfactory theoretical explanation for essentially

† This situation can be understood qualitatively because the spin part of the matrix element is negligibly small for E1 transitions while the space part (radiation due directly to the acceleration of charge) is very much the same for a 'radiating proton' or 'radiating neutron' (the 'effective charge' concept) owing to the contribution from the charge on the rest of the nucleus. For, say, an M1 transition, however, the spin contribution is large and, since the magnetic moments of neutron and proton are very different we have very different contributions from the 'radiating proton' and the 'radiating neutron'.

the same value of the intermediate coupling parameter a/K . These data are: (i) the energy of the first odd parity excited state ($3/2^-$) at 3.68 mev in ^{13}C and 3.51 mev in ^{13}N ; the magnetic moment of the ground state of ^{13}C ; the beta-decay between the ground states; the reduced nucleon width of the $3/2^-$ state of ^{13}N ; the speed of the M1 transition to ground from the $3/2^-$ state of ^{13}N . All these data are accounted for at a/K values between 4.8 and 5.5†.

Fig. 1

Level scheme of ^{13}C .

The purpose of this paper is to estimate the strength of the corresponding but non-mirror M1 transition from the $3/2^-$ state of ^{13}C at 3.68 mev to the $1/2^-$ ground state and to compare it with the same IPM calculation as accounts for the transition in ^{13}N . If the calculation is satisfactory (and charge-symmetry holds) the transition in ^{13}C should be explained by the IPM theory for the same a/K value as is required in ^{13}N .

The ^{13}N transition has a width of about 0.7 ev (Seagrave 1951) and so we anticipate that the lifetime of the corresponding ^{13}C transition will be much too short for direct measurement. The state is accessible to resonance fluorescence but this technique is difficult to use in this case. In this paper we estimate the radiative width by an application of the rule, enunciated above, that E1 transition strengths are the same in mirror

† See Lane (1955) for remarks on the comparative insensitivity of these results to other details of the calculation such as the L/K value and the exchange mixture. See however Skyrme (1958) for comments on some difficulties.

nuclei. Refer to fig. 1. The gamma-ray labelled γ_2 is an E1 transition whose mirror transition in ^{13}N , between the 3.51 mev and 2.37 mev states, has a measured width (about 0.04 ev; Woodbury *et al.* 1954). We may now transfer this reduced speed to ^{13}C and so by a measurement of the branching ratio of γ_2 versus γ_1 determine the speed of the M1 transition γ_1 .

§ 3. EXPERIMENTAL DETAILS

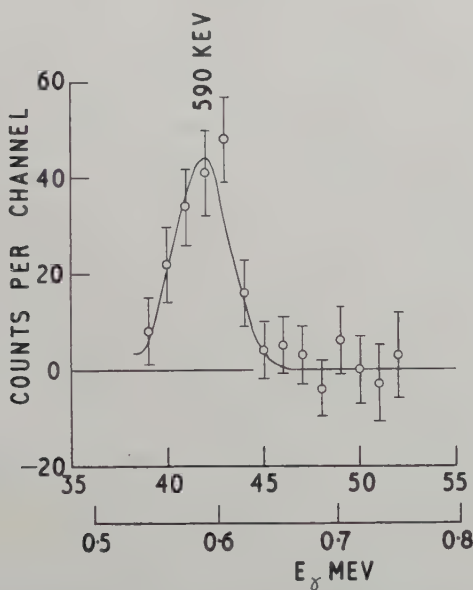
We seek to prepare the 3.68 mev state of ^{13}C in a well-defined manner and to measure the relative intensity of its cascade de-excitation. This latter probability is already known to be very low ($< 3\%$) from the work of Mackin *et al.* (1956). The state may be conveniently reached using the reaction $^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$ but the relative populations of the various ^{13}C states have not been well studied and this bombardment has the added disadvantage of producing large quantities of neutrons which are always a nuisance when gamma-ray measurements of some delicacy are to be attempted. We have chosen to use the reaction $^{10}\text{B}(\alpha, \text{p})^{13}\text{C}$. At the well-studied 4+ resonance at $E = 1.64$ mev (Shire *et al.* 1953, Stanley 1954) the proton cross sections for directly populating the 3.85 mev and 3.68 mev states are respectively 52 and 2.4 mb while the total neutron-producing cross section from $^{10}\text{B}(\alpha, \text{n})^{13}\text{N}$ is only 3.2 mb. The 3.68 mev state is chiefly populated indirectly via the 170 kev E1 transition from the 3.85 mev state labelled γ_4 in fig. 1 which constitutes 0.24 ± 0.05 of the transitions from the 3.85 mev state (Mackin *et al.* 1956).

Our experiment consisted in searching for coincidences between γ_2 and the subsequent 3.1 mev gamma-ray and comparing their abundance with the γ_4 - γ_1 coincidences. Since the 3.68 mev level is populated chiefly via γ_4 the rather large error in the γ_4 - γ_3 branching ratio is not reflected in the accuracy with which we determine γ_2 versus γ_1 . γ_4 is used as a tracer for γ_1 and we do not have to compare absolute coincidence rates with absolute single counting rates as we should had we chosen conditions in which the 3.68 mev level were populated chiefly directly. There is, however, a penalty to be paid for the use of this trick. An alternative transition from the intensely-populated 3.85 mev state is the E2, not marked on fig. 1, to the $1/2+$ state at 3.09 mev. This is of higher energy than γ_2 and will also be found in coincidence with the 3.09 mev transition; if, therefore, it were much more intense than γ_2 it would constitute a severe obscuration. In fact it is somewhat more intense, but not greatly so and can be subtracted with good accuracy from the gross high-low coincidence distribution. Its study will be described in another publication: it has no points of interest in common with the gamma-rays of our present report.

A light air-cooled target assembly bore a separated elemental ^{10}B target of measured thickness approximately 40 kev for alpha-particles of 1.6 mev. The neighbouring resonances to that at 1.64 mev are at 1.52 and 1.68 mev. The 1.64 mev resonance has a laboratory width of about 20 kev; the widths of its neighbours on the high and low energy sides are about 7 and 20 kev respectively. The yield from the desired resonance was thus optimized while giving it rather complete separation from neighbour states.

The high energy gamma-rays were detected in a 5 in. $\times$ 5 in. cylindrical NaI(Tl) crystal placed at approximately 80° to the alpha particle beam. A lead collimator in the form of a hollow truncated cone of height $2\frac{1}{4}$ in., base diameter $1\frac{3}{4}$ in. and entrance diameter $\frac{1}{2}$ in. was placed directly in front of this crystal. The entrance to this collimator was $7/16$ in. from the centre of the ^{10}B target. The low energy gamma-rays were detected at 90° to the alpha-particle beam, opposite the high energy detector, in a 3 in. $\times$ 3 in. cylindrical NaI(Tl) crystal whose front face was $7/16$ in. from the centre of the ^{10}B target. A coincidence resolving time of about $0.1 \mu\text{sec}$ was used and a convenient beam current was found to be $1 \mu\text{A}$.

Fig. 2



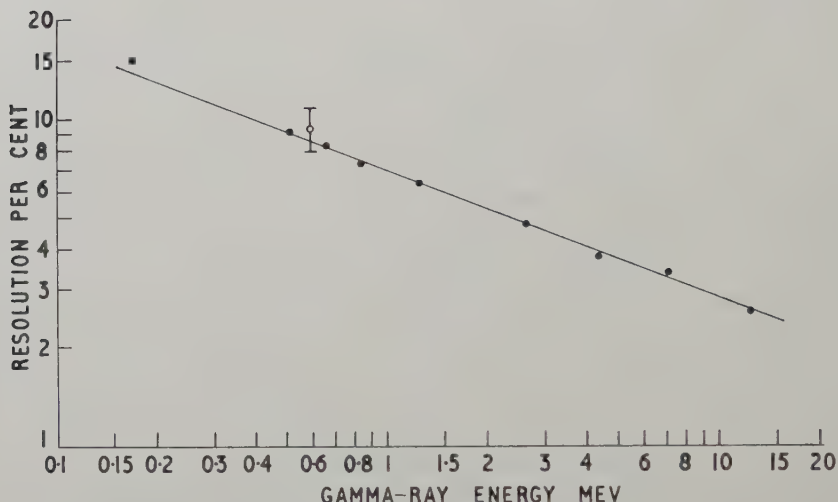
590 keV transition between the 3.68 and 3.09 meV states of ^{13}C seen in coincidence with gamma-rays of energy greater than 1.55 meV. The 765 keV transition between the 3.86 and 3.09 meV states seen in coincidence at the same time has been subtracted out.

A large number of coincidence runs was taken, displaying the coincidence counts in the 3 in. $\times$ 3 in. crystal on a bias of 1.55 meV in the larger crystal. The beam current was held constant to better than 5% during this set of runs. The bias on the large crystal as well as its response to a number of gamma-rays of both lower and higher energy than those of interest here were accurately determined since the quantitative interpretation of the results depends on a knowledge of the relative efficiency of the larger crystal, above its bias, to gamma-rays of 3.1 and 3.7 meV.

Calibration runs for the smaller crystal were made using several standard sources placed successively at the position of the target. The first purpose

of these runs was to provide an accurate energy calibration of the crystal (for this purpose the alpha-particle bombardment continued at its usual level to avoid any possible effect of rate-dependent gain—the calibration sources made only a slight change in the current in the photomultiplier). The second purpose was to determine the shape of the pulse distribution for various monochromatic gamma-rays to enable an accurate decomposition of the coincidence spectrum to be made (for this purpose there was no beam on the target and the ^{13}N was allowed to die away).

Fig. 3



Experimentally-determined resolution (full-width at half-maximum) of the 3 in. $\times$ 3 in. NaI(Tl) crystal shown as the full-points. The observed width of the line of fig. 2 is shown as the point with the error limits.

The coincidence spectrum in the smaller crystal revealed clear peaks at 508 ± 7 kev, 590 ± 15 kev and 765 ± 8 kev. The first is due to annihilation radiation, the second compares well in energy with the 595 ± 9 kev expected for γ_2 and the third with the 765 ± 12 kev expected for the E2 transition between the $5/2+$ and $1/2+$ states (Ajzenberg-Selove and Lauritsen 1959). The measured shapes of the pulse distributions in the smaller crystal were used to construct that to be expected for the 765 kev transition which was then subtracted from the gross distribution to reveal that shown in fig. 2. This distribution does not go below channel 39 since then the effect of the annihilation radiation becomes severe (a slight allowance for this has to be made also in channels 39 and 40). The accurate agreement in position of this peak with that expected leaves little doubt that it is real. As a further check we may compare the observed width of the distribution of fig. 2, namely $(9.2 \pm 1.3)\%$ with that to be expected from the known performance of the crystal. Figure 3 shows this comparison from which we see that the distribution of fig. 2 fits in very well.

§ 4. RESULTS

The peak of fig. 2, compared with the very much more intense 170 keV γ_4 - γ_1 coincidence peak gives us the γ_2 versus γ_1 branching ratio after suitable correction for peak-to-total ratios, relative absorption efficiencies of the various radiations in the smaller crystal, the slightly different efficiency of the larger crystal above the 1.55 mev bias for the 3.1 and 3.7 mev lines, the direct feeding of the 3.68 mev state by the proton transition and a few insignificant effects of absorption in the target assembly, crystal covering and so on. The angular correlations involved can be computed from data in the literature which fix the channel spin ratios (Stanley 1954): they are not strong and are effectively integrated out by the very bad geometry ($\pm 74^\circ$) of the smaller crystal. The final value for the relative strength of the cascade de-excitation is $(6.5 \pm 1.0) \times 10^{-3}$, consistent with the earlier limit.

The radiative width of the mirror E1 transition was computed from the data presented by Woodbury *et al.* (1954) as 0.04 ev. Our earlier discussion in §§ 1 and 2 implied that the reduced speed corresponding to this width may be directly transferred to ^{13}C and applied to the mirror transition. This is not quite true however because the corresponding states in the two nuclei are not quite true mirror states: in ^{13}C they are both bound while in ^{13}N they are both in the continuum. In terms of the proton capture by ^{12}C to form the $3/2^-$ state of ^{13}N both the regular (F) and irregular (G) parts of the proton wave function resonate and contribute to the radiative width. In the corresponding case of ^{13}C the contribution from the exterior region (F) is quite different and presumably much smaller than for ^{13}N since the neutron wave function cuts off sharply from the nuclear surface owing to the binding whereas the proton wave function is not cut off. We should therefore take that portion of the radiative width in the ^{13}N case that is associated with G and transfer this to ^{13}C as a measure of the transition speed there rather than use the whole width. The separation of the F and G contributions is not simple and leads to large uncertainties but it seems likely that that part of the width in ^{13}N associated with G lies between 0.02 and 0.035 ev. We are very grateful to Professor R. F. Christy of the California Institute of Technology for drawing our attention to this very interesting effect.

When these figures are transferred to ^{13}C and corrected for the different energy of the transition they imply, together with the presently measured branching ratio, a width for the ground state M1 transition from the 3.68 mev level of:

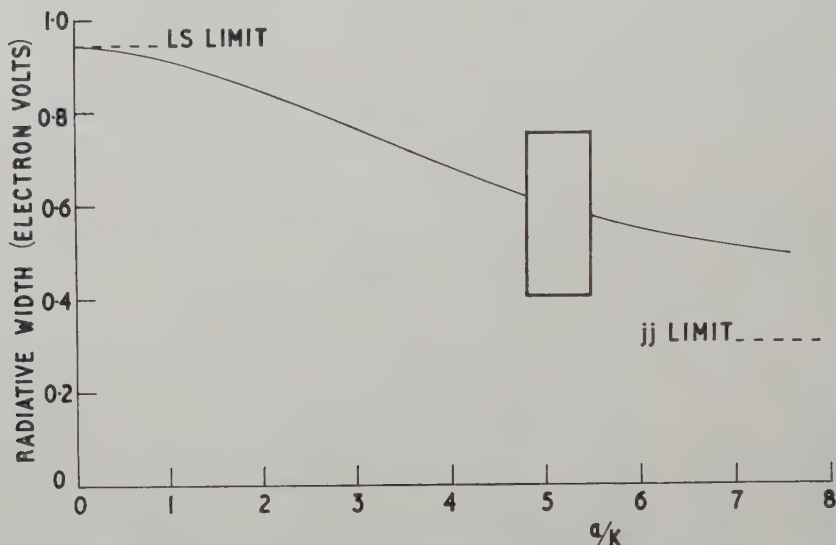
$$\Gamma_\gamma = (0.40-0.75) \text{ ev.}$$

§ 5. DISCUSSION

We may now compare this result with the IPM theory. This latter has been very kindly furnished by Dr. Dieter Kurath of the Argonne National Laboratory, whom we thank. Figure 4 shows the calculated radiative

width as a function of a/K . Also shown is the value in the jj limit ($a/K = \infty$). The upper and lower limits of the heavy box are those of our present result; the sides of the box show the limits on a/K within which the other properties of the $A=13$ system discussed above are explained by the IPM. For consistency with the IPM and charge symmetry the theoretical line of fig. 4 should pass through the box as it indeed does.

Fig. 4



The prediction of the independent particle model for the M1 radiative width of the ground state transition from the 3.68 mev state of ^{13}C shown as the full line (due to Dr. D. Kurath). The heavy box shows (top and bottom) the error limits of the present measurement and (side to side) the limits on a/K needed to explain other data in the $A=13$ system.

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Microtwinning in Epitaxial Nickel-Iron Films†

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[Received October 1, 1959]

ABSTRACT

Thin films of permalloy (81% Ni, 19% Fe) grown by evaporation on rock salt cleavage faces have been studied in the electron microscope. Selected area diffraction patterns indicate the presence of microtwinning on all types of {111} planes. The diffraction patterns are also subject to the effects of multiple diffraction, film deformation, and an 'effective aperture' in the optical behaviour of the electron microscope when used for selected area diffraction. Electron micrographs reveal a 'film' that consists of discrete particles, three-dimensional in character, with irregular shapes suggestive of hemispheres of various sizes which have coalesced, side by side. The irregular shapes fit together like pieces of a jig-saw puzzle to cover the film area. Twinned components can be identified with dark field illumination. The three-dimensional particles seem to be a consequence of isotropic growth of crystal nuclei that are in epitaxial orientation but distributed at random over the substrate surface. Microtwinning appears to be a relief mechanism for reduction of the strain energies which accumulate at the boundaries between growing crystal nuclei.

§ 1. INTRODUCTION

THE magnetic properties of thin, evaporated films of alloys of nickel and iron are of considerable interest for switching applications. The parameters of interest such as coercive force and anisotropy are unfortunately quite difficult to control within the limits desired. The work described herein was a direct consequence of an investigation into the effect of the substrate on the magnetic properties of the deposited films. The alloy of interest here is permalloy with nearly zero magnetostriction (81% Ni, 19% Fe) and the substrate is a freshly cleaved NaCl single crystal. The magnetic measurements will be discussed elsewhere since they are not pertinent to the structural problems posed by these films. This paper is therefore concerned only with electron diffraction and microscopy results.

§ 2. EXPERIMENTAL

Films of Ni-Fe alloy having a composition near 80:20 (Permalloy) and in the range 400–800 Å thick for this purpose were prepared by subliming a Ni-Fe alloy under carefully controlled conditions‡. The results to be discussed in this paper were obtained from films deposited

† Communicated by the Author.

‡ All evaporated films in this work were prepared by F. W. Reynolds and G. R. Stillwell.

on fresh NaCl (100) cleavages maintained at about 320°C. The time required to lay down the film was of the order of one hour.

Following evaporation, a plastic lacquer film was applied to the surface to act as reinforcement during removal†. The composite film was floated off the NaCl in water, caught on a copper mesh and then the plastic removed by immersion in a solvent. Specimens for the Siemens Elmiskop I were punched from the screen and examined in the instrument. Micrographs at 20 000 × or 40 000 × and selected area diffraction patterns using a 50 μ aperture were taken using 100 kv electrons.

Figure 1 (Pl. 35) is representative of the micrographs from a film deposited at 320°C and does not appear even to approximate a single crystal. Selected area diffraction patterns indicated a gross approximation to a single crystal with a cube face in parallel orientation to the base NaCl. The alloy is face-centred cubic with $a \approx 3.55 \text{ \AA}$.

The appearance of the selected area patterns varies considerably over the area of the film due to local bending and sagging of the film between wires of the support grid. The zone axis of the diffraction pattern thus varies from point to point being usually a few degrees from [001]. When the orientation is almost coincident with the [001] axis the pattern consists of a simple square array of intense spots. Patterns have also been obtained with the orientation inclined by as much as 11° to the [001] axis. However, the most interesting and informative patterns occur at intermediate orientations of about 5° to 7°. Figure 2 (Pl. 36) is typical of such patterns. A primary array generated by 200 and 020 vectors is discernible in the central region of the pattern. However, many of the integer points such as the rows of $2k0$ and $\bar{2}k0$ are surrounded by four extra spots. Other integer points such as the rows $4k0$ and $\bar{4}k0$ are very weak and form part of a new square array whose edges are parallel to the 220 and $\bar{2}\bar{2}0$ vectors. The spots along these diagonals are spaced at intervals of one-sixth of the 220 vector. This complex array arises from the f.c.c. alloy as evidenced by the spotty f.c.c. rings which intersect the orderly array of spots.

An important factor to be taken into account in all selected area patterns is the fact that regions of the specimen near the edge of the selected area aperture do not contribute uniformly to the entire diffraction pattern. Rather, a region near the edge produces only a partial diffraction pattern. The asymmetry present in patterns such as fig. 2 indicates that this must be so. The effect can be observed directly if a specimen is adjusted so that it just projects along one edge of the selected area aperture. A regular array of spots or rings will be recorded over a limited sector of the pattern while the remainder is blank. As the projection of the specimen in the aperture is increased the size of the sector increases. If the foil is moved to cover half or more of the selected area aperture, the diffraction pattern becomes more nearly normal in that a full field is seen. However, in

† The technique of removal and handling was carried out by Miss S. E. Koonce.

interpreting intensities in these patterns, it must be kept in mind that each element of volume of the sample does not contribute uniformly to the entire diffraction pattern but maintains a geometric relation with a portion of the pattern. The instrument behaves as though there were an extra aperture between the lens system and the photographic plate. Such an aperture would transmit only a fraction of the diffracted beams originating near the periphery of the selected area†.

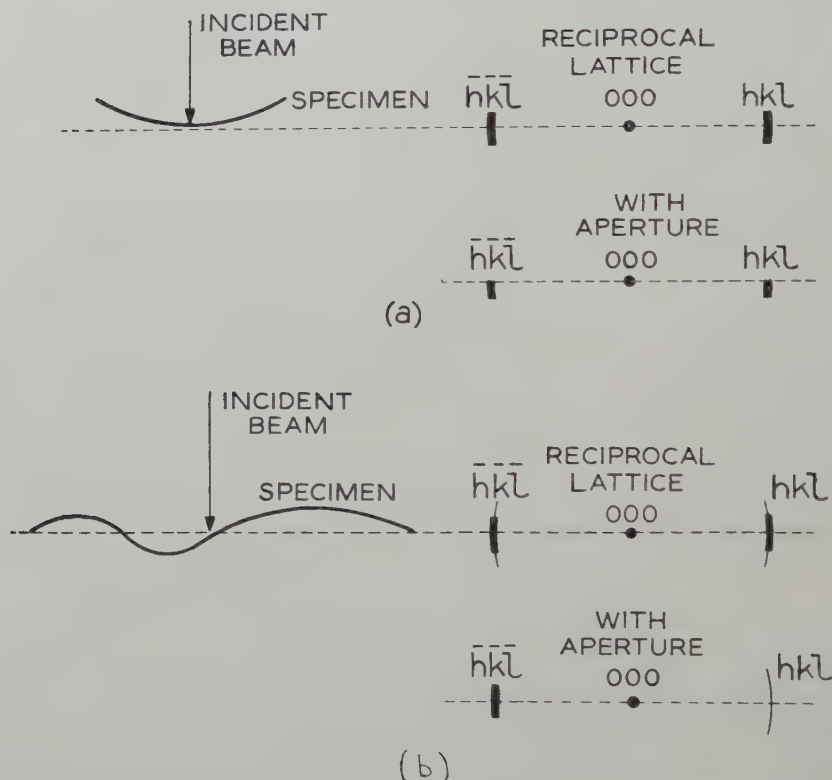
§ 3. INTERPRETATION OF SELECTED AREA DIFFRACTION

The instrumental response discussed in the previous section has several consequences that must be considered when dealing with films which deviate from planarity. In fig. 3 (*a*) a foil is shown which is deformed into a portion of a cylindrical surface of constant radius. The cylinder axis is normal to the plane of the figure. In the reciprocal lattice the points hkl and $\bar{h}\bar{k}\bar{l}$ have become short arcs. With the 'effective aperture' in place only the lower half of each arc can be transmitted. The horizontal dotted line represents the mean plane of the specimen and the plane of the zero level of the reciprocal lattice. If the 'plane of reflection' (a more descriptive term than 'sphere of reflection' for 100 kv electrons) is inclined at a slight angle to the plane of the zero level it is quite possible for hkl to reflect strongly while $\bar{h}\bar{k}\bar{l}$ is absent. Figure 3 (*b*) illustrates a more general cylindrical deformation. The effect on the reciprocal lattice points is obvious. In all deformations of this type the arcs of the reciprocal lattice points will be normal to the plane of reflection. Consequently, the diffraction patterns, although asymmetric will consist of spots rather than streaks. Metal foils may deform in ways that will produce bumps, hollows, or saddle points. If so, the reciprocal lattice points will become curved surfaces like spherical caps. The surfaces will again be normal to the plane of reflection. If the entire specimen contributed uniformly to the diffraction pattern it would display streaks or arcs. However, when only a limited region of the specimen contributes to a particular region of the diffraction pattern it is likely to display only spots. Because of the 'effective aperture' any given interpretation of a diffraction pattern will apply to only a restricted portion of the pattern if the film is non-planar.

† We are grateful to Dr. M. J. Whelan for directing our attention to a paper to be published by A. W. Agar on the accuracy of selected area microdiffraction in the electron microscope. Agar examined in a systematic manner how specimen areas *outside* the area defined by the selector aperture contribute to the observed diffraction because of spherical aberration in the objective lens. Agar did not consider the effects obtained when only part of the selected area is filled by the specimen. We believe that a systematic examination of how specimen areas *inside* the selected area contribute to the observed diffraction would show that spherical aberration also causes what we have loosely called an 'effective aperture'. It is apparent that a definitive interpretation of a diffraction pattern must take account of *all* contributions from both inside and outside the area defined by the selector aperture.

It is well known that twinning on all four $\{111\}$ planes is characteristic of epitaxial growth of most of the f.c.c. metals on NaCl (see for example the excellent review article by Pashley (1956)). The effect of twinning on the reciprocal lattice is to produce a compound lattice consisting of the original lattice plus the superposition of four twinned lattices. A portion of such a compound lattice is illustrated in fig. 4. The view is along the $[001]$ direction of the original lattice. The triple integers are Miller indices of points in the parent lattice. The single integers indicate coordinates along the $[001]$ direction in units of one-sixth of the 002 vector.

Fig. 3

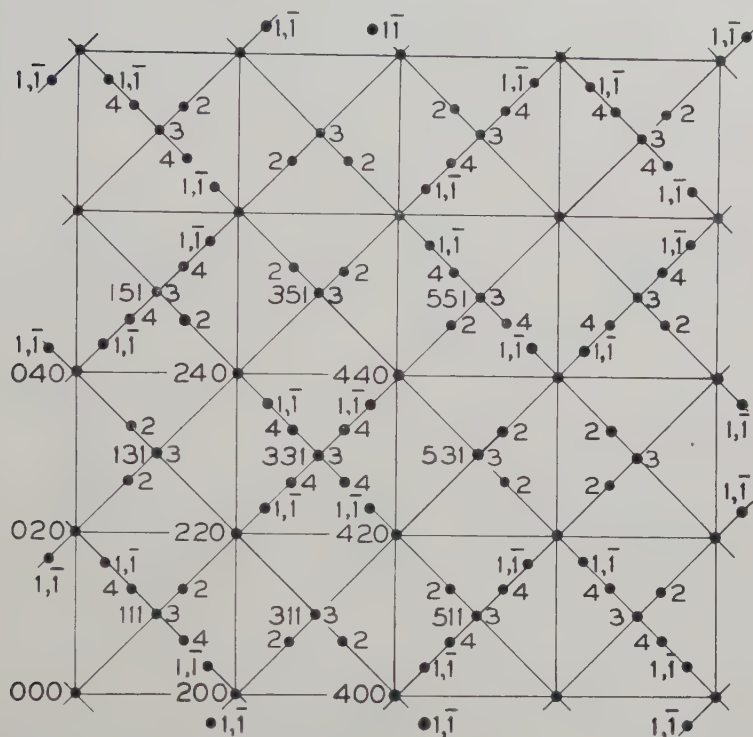


Formation of asymmetric diffraction pattern when a non-planar specimen is subjected to the 'effective aperture' of the electron microscope. (a) Simple cylindrical deformation. (b) More general cylindrical deformation.

The type of pattern shown in fig. 2 is caused by several factors including film deformation, inclined plane of reflection, double diffraction and an 'effective aperture'.

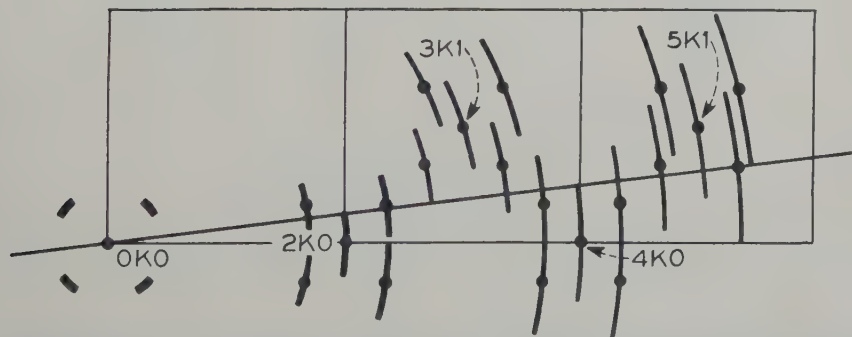
To see the effects of a deformed film and inclined plane of reflection consider fig. 5. The view is along the $[010]$ direction of the compound

Fig. 4



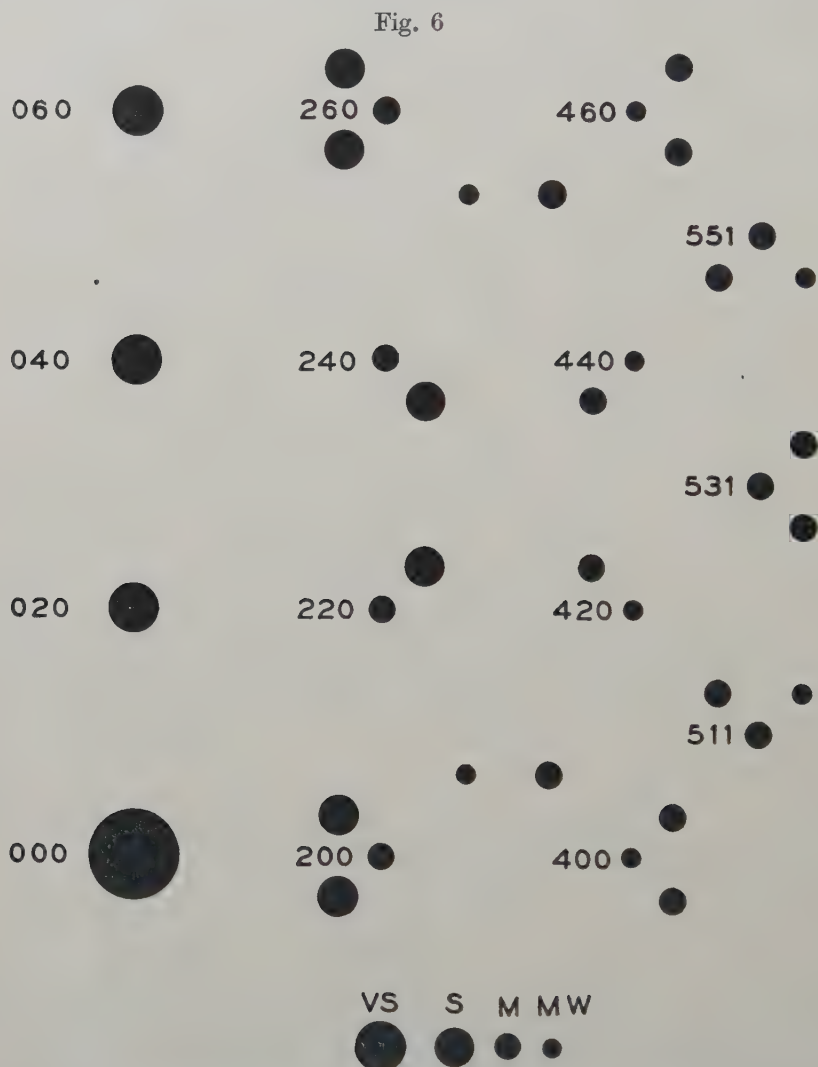
Compound reciprocal lattice formed from twinning on (111), ($\bar{1}\bar{1}1$), ($1\bar{1}\bar{1}$), and ($\bar{1}11$) planes. View along [001] zone axis. Triple integers are Miller indices of parent spots. Single integers indicate coordinates of spots along [001] in units of one-sixth of the 002 vector.

Fig 5



Lattice of fig. 4 viewed along [010] direction. Plane of reflection inclined at 7° to the zero level. Spots spread into arcs by cylindrical deformation of specimen of $\pm 7^\circ$.

lattice of fig. 4. Rows of spots are seen end-on and rows of integer spots are labelled as $0k0$, $2k0$, $3k1$, etc. The film is given a cylindrical deformation of $\pm 7^\circ$ with the cylinder axis along the $[010]$ direction. The plane of reflection is inclined at 7° to the plane of $hk0$ reflections. Each lattice point is spread into an arc whose length varies directly with the distance

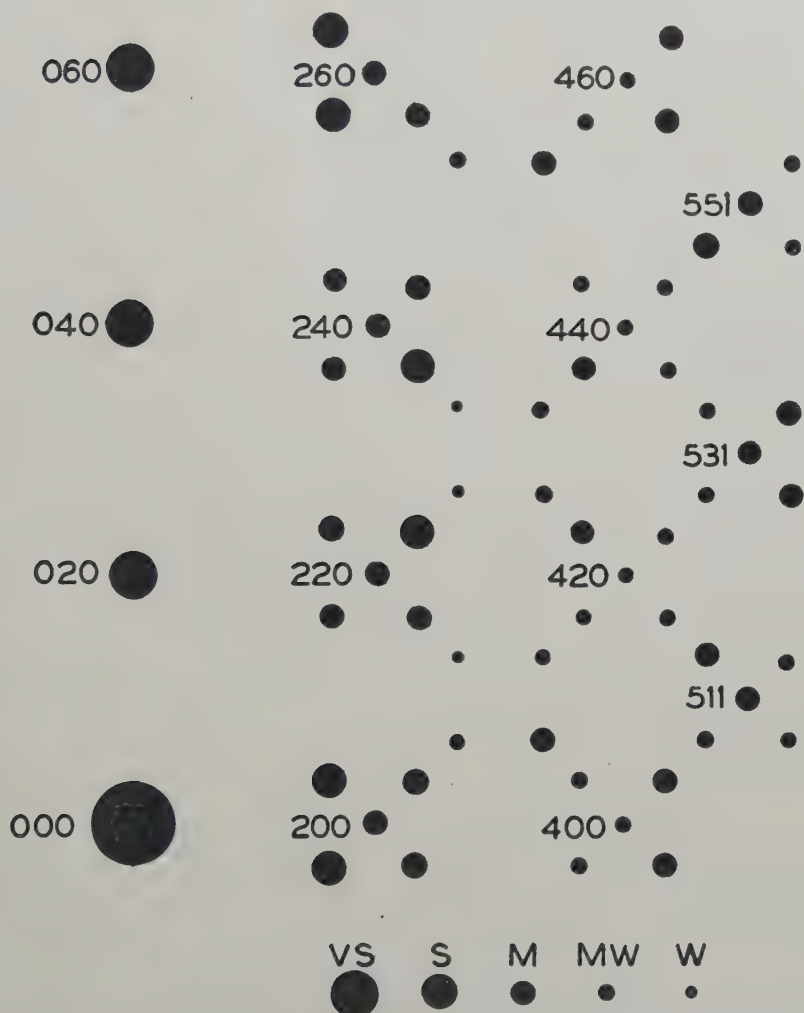


Diffraction pattern predicted when effects of fig. 5 are combined with fig. 4.

of the lattice point from the origin. The arcs fall on a series of cylinders concentric around the origin. All points of fig. 4 are assumed to have the same intensity before arcing. After arcing assume a very strong intensity on the innermost cylinder, strong on the next three cylinders, medium

on the remainder. When an arc just touches the plane of reflection assume its intensity falls one grade. Thus, assign medium intensity to the $2k0$ arc, medium weak intensity to three other arcs.

Fig. 7



Diffraction pattern predicted from fig. 6 by double diffraction from 020 and $0\bar{2}0$ reflections. Compare with upper right quadrant of fig. 2.

Combining the effects of fig. 5 with fig. 4 the pattern of fig. 6 is obtained. This represents the effects of microtwinning, film deformation, and inclination to the plane of reflection. Now consider the effect of double

diffraction on fig. 6. Assume that when two reflections occur in succession the intensity of the double reflection is as follows:

$vs + s \rightarrow m$	$s + s \rightarrow mw$	$m + m \rightarrow vw$
$vs + m \rightarrow mw$	$s + m \rightarrow w$	$m + mw \rightarrow vvw$
$vs + mw \rightarrow w$	$s + mw \rightarrow vw$	
$vs + w \rightarrow vw$	$s + w \rightarrow vvw$	
$vs + vw \rightarrow vvw$		

Every reflection in fig. 6 is the source of a new incident electron beam. By superposition† of all the new patterns created the total effect of double diffraction is obtained. The major part of the effect is obtained by considering only very strong reflections. In fig. 7 the result is shown of superposing fig. 6 with the reflections obtained by double diffraction from the 020 and 0 $\bar{2}$ 0 reflections. A considerable area of this pattern agrees very well with the upper right hand quadrant of fig. 2.

The other regions of fig. 2 do not agree with fig. 7 because the deformation of the specimen film is not of a cylindrical form parallel to [010] except in the central region of the specimen. The appearance of the 040 and 060 reflections in fig. 2 suggests that there is a cylindrical deformation parallel to [100] in the outer region of the specimen. At its simplest the deformation of the film must be of an oblong dish shape or a saddle shape.

Some of the earlier workers who observed microtwinning of f.c.c. metals on rock salt did not take account of double diffraction (see for example Menzer (1938a, b) and Göttsche (1953)). To explain the non-integral spots which do not arise directly from twin orientations they postulated microstructures that would give the scattering power of the (111) planes a periodicity three times that of a normal lattice. However, as long ago as 1940 Thirsk and Whitmore stated that the non-integral spots which do not arise directly from twinning could be accounted for by double diffraction.

§ 4. ELECTRON MICROSCOPY OF MICROTWINNING

Figure 1 is a typical micrograph of a 'thick' film in the 400–800 Å range taken with bright field illumination. The film appears to be made up of particles that tend to be equidimensional, ranging from 300–700 Å in diameter. There are a variety of contrast effects including regular fringe systems over very limited areas. Figure 8 (Pl. 37) is a micrograph of a thick film taken with dark field illumination containing both twin spots and double diffraction spots. It would appear that a large fraction of the film belongs to twinned lattices, possibly 30 to 40%. Many of the details observed in fig. 8 are presumably Moiré patterns formed by the double diffraction spots in the illumination.

† The superposition consists of a translation, without rotation, from 000 to the point being considered as a new incident beam.

The absence of any simple pattern in figs. 1 and 8 suggests that the thickness of the film has caused an excess of details to overlap. Films were then chemically etched to an estimated 100–200 Å thickness. Figure 9(a) (Pl. 38) shows a bright field micrograph of such an etched film. Figure 9(b) shows a corresponding dark field micrograph. The illumination contained twin spots from two of the four twinned lattices and a negligible component of double diffraction. Several twinned regions in fig. 9(a) are indicated by numbered arrows. Their identification as twins is confirmed by comparison with the corresponding regions in fig. 9(b). A region such as that indicated by arrow 1 has dimensions of the order of $500 \text{ Å} \times 750 \text{ Å}$. Arrow 4 indicates a region of twin bands that are approximately 50 Å wide.

'Thin' films in the 100–200 Å range were then made by direct sublimation. Figure 10 (Pl. 39) is typical of the resulting microstructure. The film consists of discrete particles, three-dimensional in character, with rather irregular shapes. Many of the shapes are suggestive of an agglomeration of hemispheres of various sizes which have coalesced, side by side in one plane. The irregular shapes fit together to cover the area of the film in the same manner as the pieces of a jig-saw puzzle. In a few places a sequence of parallel twin bands is observed. The twin bands run about 25 Å in width. Figure 11 (Pl. 40) is a more limited area of thin film at higher magnification. Contrast details down to 10 Å or less are distributed in an irregular manner throughout the micrograph.

The various electron micrographs do not provide any simple picture of the microtwinning. Twinned regions can be recognized but they occur in no recognizable pattern. The width of a twinned region can apparently vary from 25 Å to 500 Å. The contrast details observed in the micrographs arise from a complex mixture of effects of crystal thicknesses, dynamic interactions, multiple diffraction, twin boundaries, etc.

The following features of the epitaxial growth appear to be consistent with the microscopic and diffraction evidence:

1. The nuclei are distributed at random over the substrate surface.
2. The nuclei undergo three-dimensional growth.
3. The principal influence of the substrate is maintaining a parallel orientation between the two cubic phases.
4. The misfit in lattice spacing of the two cubic phases is of minor importance.
5. The lattices of the nuclei have no optical phase relation with the lattice of the substrate.
6. The most important strain energies are intra-phase rather than inter-phase, i.e. intergranular rather than between film and substrate.

In a general way the process of film growth and microtwinning can be suggested from the considerations listed above. The nuclei grow isotropically. Ultimately contact will occur between a given pair of nuclei.

Only in rare instances will there be an integral lattice vector separation between the nuclei. In general then, a boundary of increasingly higher energy will be formed as the nuclei come into contact and continue to grow. The strain energy will accumulate to provide the driving force for the possible occurrence of faulting, twinning, recrystallization or other relief processes. With a random distribution in size of nuclei one of a given pair will usually be larger than the other and will probably be more firmly anchored to the substrate, and hence more stable. If the difference in stability between a pair of nuclei and the boundary energy both become sufficient then the larger grain may assimilate the less stable one. This might occur in a variety of ways. However, in view of the experimental evidence the conditions would appear to be especially favourable for the widespread occurrence of microtwinning on all $\{111\}$ planes. Presumably only one orientation of $\{111\}$ would be active at a particular grain boundary. Stacking fault energies must be low and the driving forces high under the conditions of the experiment. The transition from vapour state to epitaxial growth is equivalent to quenching in an extreme form. Hence it is not surprising that the driving forces are readily available in the energy built up in the grain boundaries.

Reflection electron diffraction patterns from 600–800 Å epitaxial Ni-Fe films indicate that the microtwinned material occurs as a sandwich between the sodium chloride on the one side and single crystal alloy on the top side. Apparently the layer of twinned material serves the purpose of accommodating the cubic alloy to the cubic substrate with minimum strain energy. From this point of view it would not be surprising if microtwinning were widespread at the interfaces in diffusionless transformations in bulk alloys. Thin sections of transformation products in steels have been observed to exhibit a fine line structure in martensitic plates (Kelly and Nutting 1959, Nishiyama *et al.* 1959) which may well be microtwinning.

ACKNOWLEDGMENTS

We wish to express our thanks to F. W. Reynolds and G. R. Stillwell for the preparation of the evaporated films used in this work, and to Miss S. E. Koonce for the preparation of specimens for the electron microscope.

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Eutectic Compositions and Liquid Immiscibility in Certain Binary Alloys†

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[Received November 3, 1959]

ABSTRACT

An examination is made of the compositions of eutectic points in the metallurgical equilibrium diagrams given in Hansen's text-book on *The Constitution of Binary Alloys*. A large number of eutectics occur at almost 0% of the solute element. With increasing atomic percentage of solute, the number of eutectics in a given composition range diminishes rapidly, until a recovery sets in at 8–10 atomic % solute. There are very few eutectics in the equiatomic region, and at intermediate compositions the eutectic composition distribution curves show a series of peaks at intervals of 7–8 atomic %. Stockdale's suggestion that eutectic points occur at whole number ratios of the two kinds of atom is not confirmed, but certain regions of composition are favoured, and these include the atomic ratios of approximately 1 : 6, 1 : 3, 1 : 2 and 2 : 3. The reason for this is discussed, and free energy curves are described; some of these lead to liquid immiscibility, and examples of this are discussed.

§ 1. INTRODUCTION

IN 1935 Stockdale (1935) suggested that, in binary metallurgical equilibrium diagrams, the compositions of eutectic points corresponded with simple whole number ratios of the two kinds of atom. Although supported by considerable evidence the idea was not accepted, partly because such large whole numbers were used that the experimental accuracy was often not sufficiently great to distinguish between adjacent possible ratios. In the meantime much accurate experimental work has been carried out, and in the present paper we re-examine the data, and discuss the results. These suggest certain types of free-energy/composition curves which, in their turn, have led to an interpretation of the phenomena of liquid immiscibility in certain alloy systems.

§ 2. EXPERIMENTAL DATA

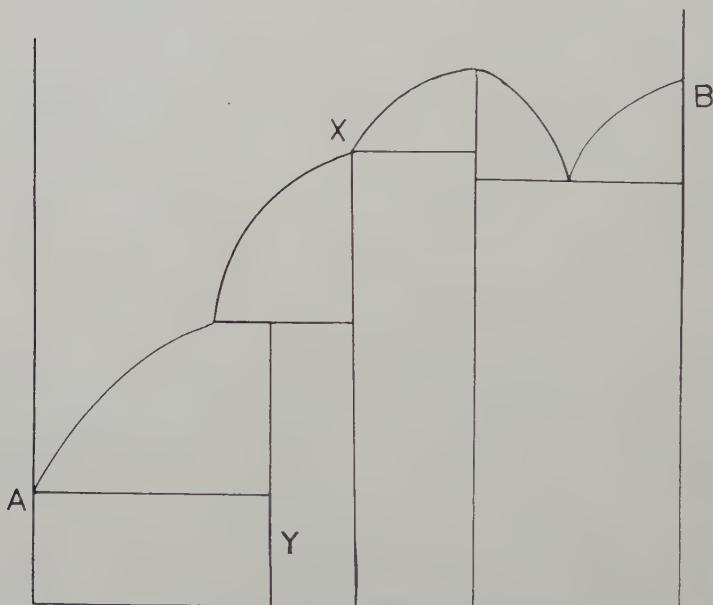
Experimental data on the constitution of binary alloys have been critically reviewed by Hansen (1958) in the second edition of his book *The Constitution of Binary Alloys*, where the composition of eutectic points which have been established with reasonable accuracy are given in atomic percentages. We have accepted these values, except in a very few cases where new experimental data are known to us. In very rare cases where

† Communicated by the Authors.

experimental points are given which establish the eutectic, we have accepted the composition, since the omission of a numerical value appears accidental. There are occasional systems of the transuranic elements for which Hansen gives a numerical value, but the text makes it clear that the whole diagram is approximate only, and these have been omitted completely. These details are discussed in the Appendix, and do not affect the conclusions described below.

Apart from these reasonably well-established (W. E.) eutectic points, Hansen's book gives many eutectics for which he gives an approximate value (e.g. ~ 12 atomic %), or where the composition is not indicated. For some purposes, these are of interest, and we have again accepted Hansen's value throughout, except that we have ignored some systems

Fig. 1



where the description makes it clear that the composition is quite uncertain. It is convenient to distinguish between the well-established (W. E.) eutectics, and the total number of eutectic points.

§ 3.

3.1. *The 0% Eutectics*

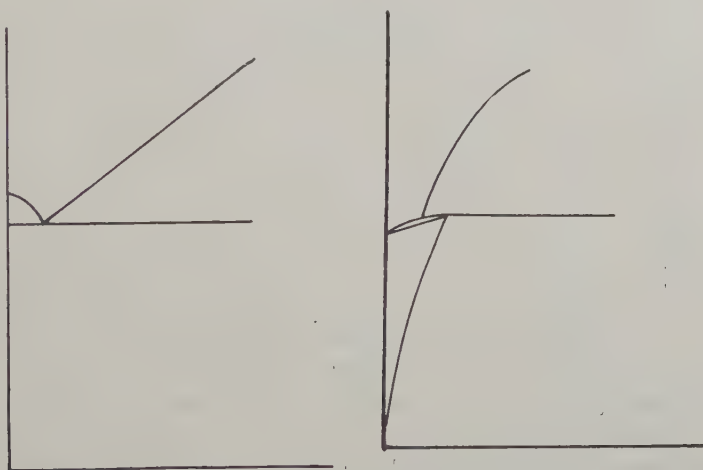
In the hypothetical diagram of fig. 1, the solidus horizontal at A is at a temperature indistinguishable from that of the melting point of the pure metal. Many such examples exist, and may be called the '0% Eutectics'. We think that these may properly be classed as eutectics, because in the cases where experimental accuracy has detected a slight difference between

the temperatures of the horizontal and of the melting point of the pure metal, the number of systems in which a slight depression of the liquidus has been found (fig. 2(a)) greatly exceeds that in which the liquidus rises to a peritectic horizontal just above the melting point of the pure metal (fig. 2(b)). The peritectic kind of diagram (fig. 2(b)) requires the solubility of B in A to be greater in the solid than in the liquid, and where the solubility is restricted this is less probable than the case of fig. 2(a).

3.2. The C.M.P. Eutectics

In fig. 1, the equilibrium relations are such that a phase *X* melts at constant temperature, but without a maximum in the liquidus. The free energy relations are of the same form if points such as *X* are regarded as the extreme limit of eutectic or peritectic diagrams, and we refer to them as 'constant-melting-point', or C.M.P. eutectics.

Fig. 2



§ 4. THE STOCKDALE HYPOTHESIS

Hansen's data for the W.E. eutectics make it clear that Stockdale's hypothesis in its original form cannot be maintained. Eutectics are distributed over a very wide range of compositions, and agreement with exact whole number ratios is an exception rather than a rule, unless unduly large integers are employed. The distribution of eutectics over the whole range of compositions is, however, very uneven, and some of the fluctuations are greater than would be expected from a random distribution.

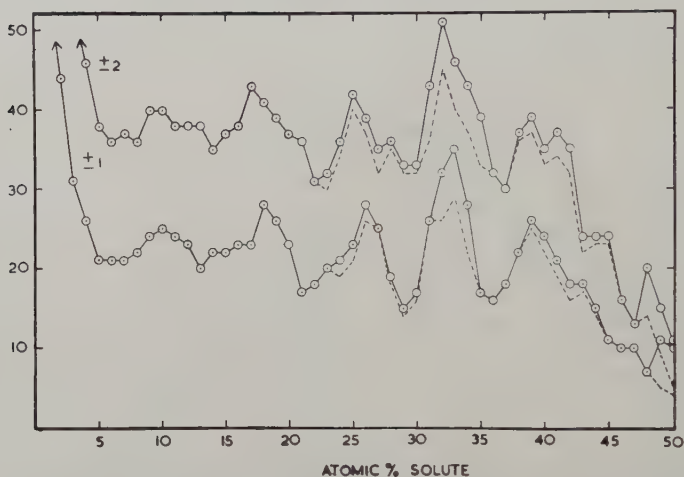
§ 5. THE EUTECTIC COMPOSITION DISTRIBUTION CURVES

To examine the problem further, we have drawn diagrams showing the number of eutectic points lying within ± 1 and ± 2 atomic % of each whole-number atomic percentage of solute. Since there is no reason why a given system should be called AB rather than BA we have expressed the compositions as lying between 0 and 50. If, for example, a particular system

AB has eutectics at 26 and 90 atomic % of B, the eutectic compositions are called 26 and 10. This procedure means that, for statistical examination, we must double the number of points at exactly 50 atomic %, and this has been done in drawing the diagrams.

Figure 3 shows the composition distribution curve for the W.E. eutectic points, and fig. 4 the corresponding curve for all the eutectic points. In fig. 3 the composition 20 atomic % corresponds to values of 23 and 37 on the ± 1 and ± 2 curves respectively, and this means that there are 23 eutectic points in the range 19–20–21 atomic %, and 37 in the range 18–19–20–21–22 atomic %. For each curve the full lines include the

Fig. 3



The eutectic composition distribution curves for W.E. eutectics.

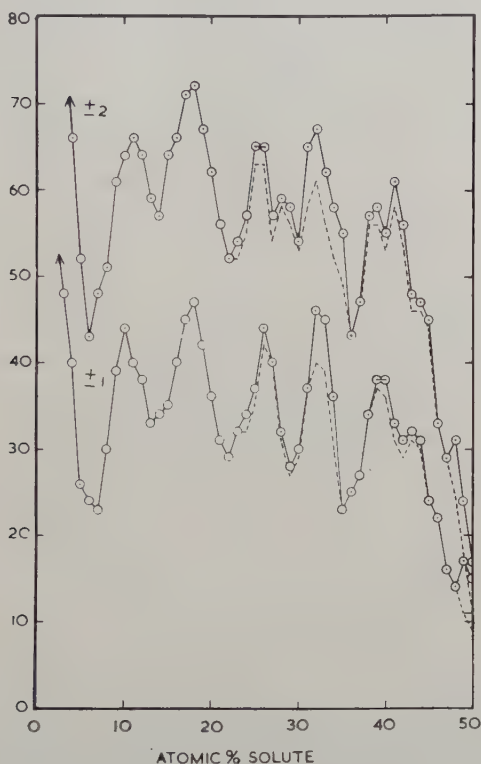
C.M.P. eutectics, and the dotted lines show how the numbers are reduced if the C.M.P. eutectics are excluded. From these diagrams the following conclusions may be drawn.

- (a) There is a very large number of 0% Eutectic Points.
- (b) With increasing percentage of solute, the distribution curve first falls rapidly, and then rises in the range 8–10 atomic %.
- (c) There are very few eutectics in the equiatomic region.
- (d) In the intervening region, the distribution curve shows a remarkable series of peaks and valleys, the peaks being separated by differences of the order 7–8 atomic %. This tendency is clearly apparent if the C.M.P. eutectics are excluded, and is accentuated by their inclusion. The magnitude and approximately regular spacing of the peaks makes it improbable that they are due to random fluctuations. The relative heights of the peaks are greater for the W.E. eutectics than for the total number. This can be understood because, if the peaks are due to a genuine effect, any error in the compositions of the eutectics will tend to smear out

the sharpness of the peaks, and to increase the general background. The last three peaks are in the regions of 25, 33 and 40 atomic %, and are thus near to the simple whole number ratios 3:1, 2:1 and 3:2.

The eutectic distribution curves of figs. 3 and 4 are admittedly statistical, and the variation of experimental accuracy makes their value difficult to assess. It has been suggested that the small number of eutectic points in the equiatomic region may be due to the existence of a large number of

Fig. 4



The eutectic composition distribution curves for all eutectic points.

intermediate phases with liquidus curves rising to maxima at the composition AB, since a maximum on the liquidus curve automatically prevents the formation of a eutectic at the composition concerned. Examination of the systems which do *not* contain AB liquidus maxima shows that this suggestion is incorrect, and that the small number of eutectic points in the equiatomic region cannot be ascribed to this cause alone. Further, examination shows that the three most common compositions giving rise to maxima on liquidus curves are AB, A_2B and A_3B . The last two of these correspond with 33 and 25 atomic % solute respectively, so that the appearance of peaks on the eutectic distribution curves at these

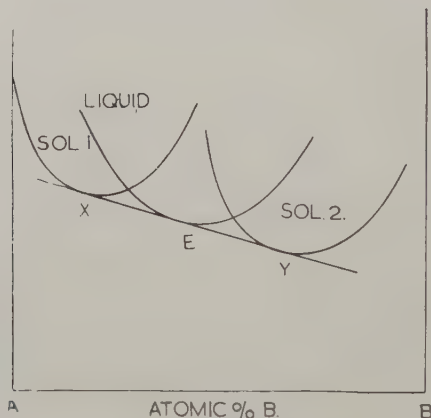
compositions is even more remarkable than might at first appear, since the existence of the A_2B and A_3B maxima on liquidus curves must tend to diminish the number of eutectics at these compositions.

§ 6. EUTECTIC FREE-ENERGY CURVES

In the typical eutectic equilibrium, the relation between the free-energy curves and compositions is of the form shown in fig. 5, where XEY is the common tangent to the curves, and E is the composition of the liquid in equilibrium with solid X and solid Y .

If, as was imagined by Stockdale, liquid alloys can take up ordered structures of the two kinds of atom, the free-energy/composition curve—for abbreviation we shall call this the G/C curve—for the liquid phase may show a minimum at the composition which enables the two kinds of atom to pack together conveniently, and we may expect this to correspond with

Fig. 5



a whole number ratio related to the geometry of the structure. Figure 5 makes it clear that the composition of the point E only occurs at the minimum on the curve if the tangent is horizontal, and all three phases have the same free energy. This is an unlikely occurrence, and we can, therefore, understand why Stockdale's hypothesis is not, in general, confirmed.

Figure 5 shows, however, that if the G/C curve for the liquid shows a rapid change in curvature at one point, tangents over a wide range of angles will strike the curve near this point, and eutectic compositions in this region will be favoured. If liquids have a structure, it may for example be possible for a liquid to accommodate a certain proportion of solute atoms easily, but for a larger proportion to result in a marked increase in free energy. The resulting G/C curve may then be of the form of fig. 6, and eutectic points in the region of X will be favoured. In such a case, if the rise in the G/C curve after X is the result of the geometry of the packing of atoms, X may correspond to a simple whole-number ratio of atoms.

Alternatively if, as in the Jones theory of α/β brasses, the bend at X is due to an electronic factor, we may expect a characteristic composition which is not a whole-number ratio.

Another possibility is for a particular ratio of the two kinds of atom to facilitate the packing of the atoms in the structure to such an extent that a marked fall occurs in the G/C curve, as shown in fig. 7. In this case, tangents over a wide range of angles can touch the curve in the region of X , whilst the inflections in the curve may result in the formation of immiscible liquids—examples of this are described on p. 397.

Fig. 6

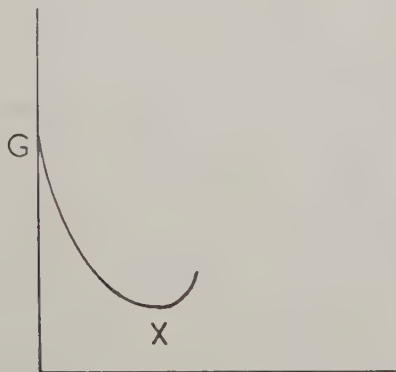
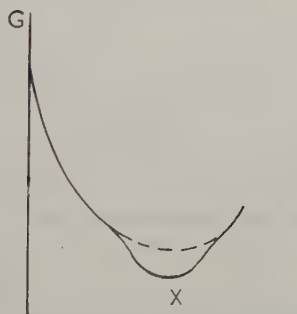


Fig. 7

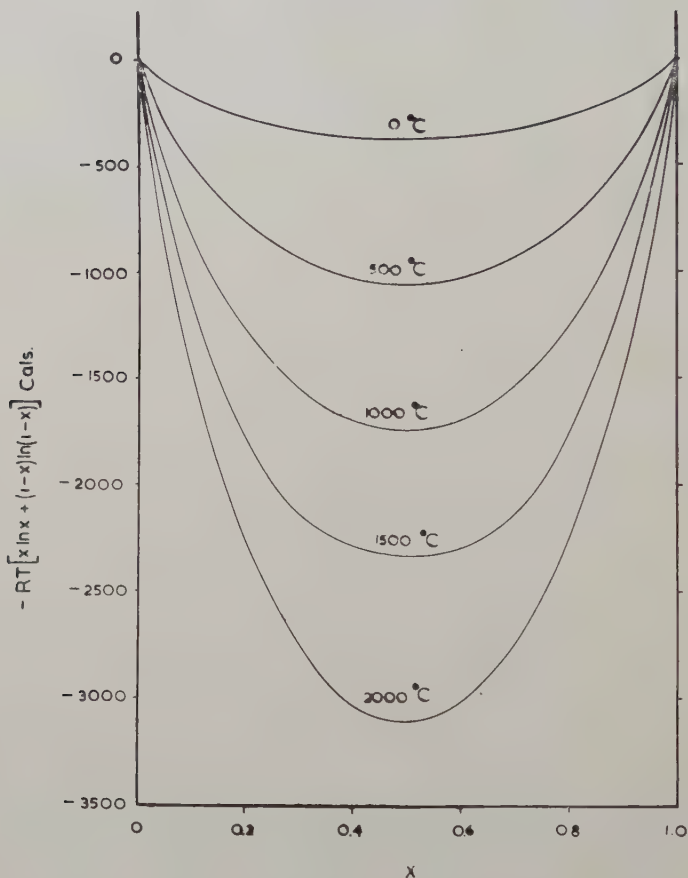


§ 7. THE 0% EUTECTIC REGION

In diagrams such as fig. 5, the free energies have to be measured with reference to arbitrary zeros for both constituents. The choice of zeros affects the slope of the line XEY in fig. 5, but not the compositions of the tangent points X , E and Y . For many purposes it is convenient to choose the zeros so that, at the temperature concerned, the values of G for the pure liquids A and B are equal. This can be done by an arbitrary choice of the zeros at each temperature, in which case the zeros change with the temperature. Alternatively we may take a fixed zero (such as the energies of isolated atoms), and denote ΔG the difference between the free energy of

the alloy concerned, and of the corresponding point on the straight line joining the values for pure A and pure B. ΔG will then be zero for pure A and B, and curves connecting ΔG with C will resemble those for curves of G against C , with zeros adjusted to make the values for the pure liquids A and B equal.

Fig. 8

 $\Delta G/C$ curves for ideal liquid solutions.

In a liquid solution the configurational entropy which results from the random mixing of A and B produces a free-energy term of the form :

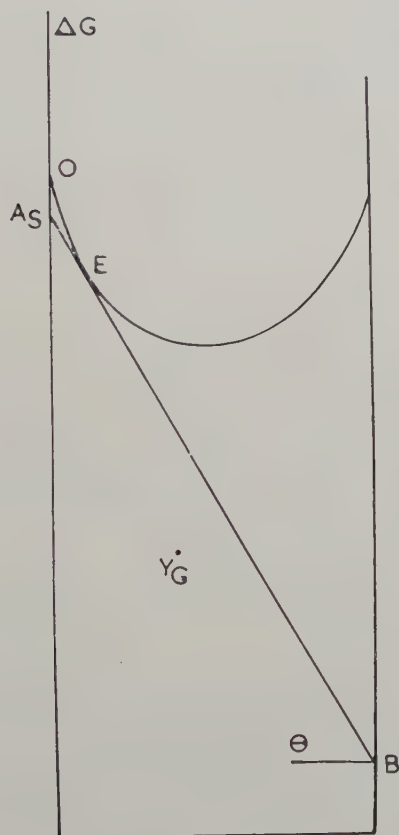
$$RT\{x \ln x + (1-x) \ln (1-x)\}$$

where x is the atomic fraction of B. This gives a $\Delta G/C$ curve (i.e. a curve of ΔG plotted against the composition in atomic fractions) which is vertical at $x=0$ and $x=1$, and is symmetrical about the equiatomic composition ($x=0.5$). Examples of these curves are shown in fig. 8. In ideal liquid solutions where there is no heat or volume change on mixing, the $\Delta G/C$

curves are of the form of fig. 8. In non ideal solutions, the $\Delta G/C$ curves will show other shapes, but as long as miscibility occurs the curves will always be vertical at $x=0$ and $x=1$.

We may consider, for simplicity, a 0% eutectic system in which the two solid phases in equilibrium with the liquid are the pure metals A and B. Since the configurational entropy term is included in the total $\Delta G/C$ curve, the tangent at 0% B will be vertical, and will not meet the ΔG curve for solid B. We may thus conclude that, if mixing of the two metals occurs, the eutectic can never be at exactly 0% solute, and we may imagine that

Fig. 9

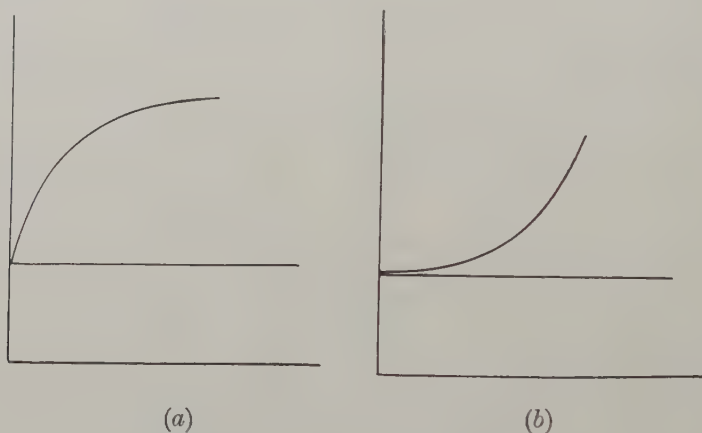


in fig. 9, the curve refers to a temperature just below the melting point of A, and that the point A_s gives the value of ΔG for pure solid A. E is the composition of the (very nearly) 0% eutectic, and the tangent AEB is very nearly vertical. For pure B, ΔG at the eutectic temperature must have a large negative value, and unless there are very abnormal effects, this means that B must be a long way below its melting point.

We expect, therefore, to find 0% eutectics mainly in systems where one metal is of very much higher melting point than the other. This is in agreement with the data, and the conclusion is irrespective of the existence of intermediate phases. Consider, for example, the system of fig. 1, where the 0% eutectic involves pure A, and the compound Y, whilst the melting point of B is much higher than that of A. Then, if fig. 9 refers to this system at the temperature of the (almost) 0% eutectic, the point B will lie considerably below 0, and if Y_G is the value of ΔG for solid Y, Y_G must lie below AB, for if it were above AB, the eutectic would consist of (B + A + Liquid) instead of (Y + A + Liquid). In such diagrams it is common practice so say that Y is an unstable compound which decomposes on melting, but the above considerations show that, at the temperature of the 0% eutectic, the nearly vertical slope of the tangent means that the value of ΔG for solid Y is large and negative.

A simple geometrical argument based on figs. 8 and 9 will show that the liquidus rising from a 0% eutectic will have the form of fig. 10 (a), and not that of fig. 10 (b).

Fig. 10



§ 8. MODELS OF LIQUID STRUCTURE

Figure 5 makes it clear that, for a given $\Delta G/C$ curve for the liquid solution, a given eutectic composition may arise by chance if the curves for the two solid phases are of the appropriate shapes and levels. In attempting to explain the eutectic distribution curves, we must therefore expect to find some exceptions if we correlate points such as X in fig. 7 with particular models of the liquid state, and the existence of exceptions does not necessarily mean that the correlation is incorrect.

Frank (1952) has emphasized the importance of the work which has shown that small drops of liquid metals can undergo marked supercooling. From this he concludes that, although the coordination number in a liquid metal is high, the atomic arrangement must be different from the cubic, or

hexagonal packing of spheres, since either of the latter would provide nuclei for the growth of the solid crystal. Frank, therefore suggests that the structure of liquid metals is based on the icosahedral packing of 12 atoms round a central atom as shown in fig. 11 (Pl. 41). The characteristic of this is that, if the model is held with one atom at the top, the central sphere is in contact with one sphere vertically above, and one vertically below, and with two sets of five spheres in horizontal planes. These last atoms are at the corners of two regular pentagons which are rotated through 36° about the vertical axis.

In this model the central sphere is in contact with its 12 neighbours, but the latter are not quite in contact with each other. For convenience we shall call these Frank units.

We also suggest that it may be possible for Frank units to join together in chains, in which one sphere is held in common between adjacent units. Figure 12 (Pl. 41) shows one of these chains which has been slightly bent so as to show the packing structure. In this case, the structure of the chain may be written 1-5-1-5-1 . . . where each central sphere is in contact with two sets of five, and with one sphere above and one below, but the side spheres are not in contact with each other. For convenience we shall refer to these as pentagonal chains.

§ 9. PEAKS ON EUTECTIC DISTRIBUTION CURVES

The considerations of § 7 enable us to understand the large number of eutectics at very small concentrations of solute, and the general form of the resulting liquidus curves. The distribution curves of figs. 3 and 4 show that, with increasing percentage of solute, there is at first a rapid fall in the eutectic distribution curve, until a recovery sets in at 8-10 atomic % of solute. If, therefore, we are correct in suggesting that a large number of eutectics is favoured by a marked bend in the $\Delta G/C$ curve, we may seek for some reason why a point such as *X* in fig. 6 occurs at the composition 8-10 atomic % of solute.

In general, when a solute B is added to a liquid metal A, mixing will be encouraged if there is a tendency for B atoms to prefer A rather than B neighbours. If a liquid consists of individual Frank units with solute atoms at their centres, we can substitute up to 1 atom in 13 (7.7 atomic %) without involving B-B closest distances of approach. We cannot, however, substitute more than 1 atom in 13 without introducing B-B contacts, unless very definite long range order exists. It is of course clear that the same conclusion would be reached if the liquid consisted of groups of 13 with a central atom surrounded by 12 others in hexagonal or cubic close-packing, but these arrangements would provide nuclei for crystallization which the Frank units avoid.

If a liquid consists of individual pentagonal chains with solute atoms down the centre of the chains, it is possible to avoid B-B contacts by a stacking sequence of the type 1-5-1-5-1-5-1-5-1-5-1 . . . , where the

bold figures 1 refer to the solute atoms. This corresponds to 1 solute atom in 12 (i.e. 8.3 atomic %).

If, therefore, a marked increase in G results from two solute atoms becoming closest neighbours, we may perhaps understand why a $\Delta G/C$ curve of the type of fig. 6 occurs with the point X at about 8 atomic % solute. It is not justifiable to claim more than a very rough approximation because, although the above argument is not affected by interchange between the outer solvent atoms of Frank units or of pentagonal chains, no allowance has been made for the sharing of atoms or for the odd atoms which may cement the units or chains together.

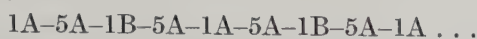
If the above interpretation is correct we may expect the sudden increase in G at the point X of fig. 6 to be favoured by a large electrochemical factor, because this will favour AB closest distances of approach. We should also expect the effect of two relatively large solute atoms in contact to produce a more marked increase in G than that of two relatively small atoms. For, in both Frank units and pentagonal chains, if a central atom is small, this may weaken the bonds to its 12 neighbours, but the remaining atoms will be able to collapse in upon each other. If, on the other hand, the central atom B is large, it may remain in contact with its 12 neighbours, but a great number of A-A distances must be increased.

If, therefore, we interpret the rise in the eutectic distribution curve at 8-10% solute on the above lines, we expect to find a preponderance of systems in which either the electrochemical factor is considerable, or in which the solute atom has a markedly larger atomic diameter than that of the solvent. As shown in table 1 this conclusion is confirmed for the 8% and 9% eutectics. We suggest, therefore, that the first break in the steeply falling eutectic distribution curve is the result of the introduction of close distances of approach between solute atoms.

If we accept the concept of a pentagonal chain, it is clear that, if the atoms down the centre of the chain were smaller than those in the pentagonal layers, those in the pentagonal layers could close up until they were in contact, and the pentagons rested on each other. This would give a packing sequence 1-5-1-5-1 . . . , where the small figure 1 indicates the smaller atom. We might thus expect a particularly stable structure with a sharp valley in the $\Delta G/C$ curve at a ratio of 1 small : 5 large atoms, i.e. 17 atomic % of the smaller atom. Figures 3 and 4 show that the eutectic distribution curves exhibit maxima in the region of 18 atomic %. Table 2 shows that if we represent the 17, 18 and 19% eutectics in the form $A_{83}B_{17}$, $A_{82}B_{18}$ and $A_{81}B_{19}$ respectively, there is a large majority of cases in which the B atom is the smaller. The above argument is again only a rough approximation, but it is at least suggestive that the peak in the eutectic distribution curve comes at approximately the ratio of 1 atom in 6.

In the above interpretation of the 18% eutectic peak, we have allowed smaller atoms down the centre of the chain to be closest neighbours, in order to allow a closing up of the pentagonal rings. We may now consider what the condition will be if no two B atoms are closest neighbours. If the

B atoms are down the centres of the chain, the best that can be done is a sequence such as :



which corresponds to 8.3 atomic % B (see p. 394). If B atoms are in the pentagonal rings, then as shown in fig. 13 one pentagonal ring can hold

Table 1

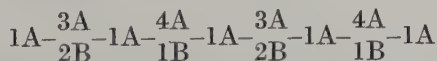
Eutectic composition	Systems with B the larger atom, and size factor (%)	Systems with B the smaller atom, and size factor (%)
$A_{92}B_8$ Total number of eutectics 11	AgTe ? CuCe 43 CuPr 43 CuU 18 ZnMg 20 AgTh 25 CuTh 41 CoZr 26	AlPd - 4 AuCd - 3 BiZn - 14
$A_{91}B_9$ Total number of eutectics 13	CuLa 47 HgTl 14 PbK 32 SnMg 14 AuLa 29 CuCa 55 NiCe 46 CrPb 40 NiU 20 SiZr 34	PbPd - 21 ZrSi - 26 USi - 22

For the $A_{92}B_8$ and $A_{91}B_9$ eutectics there are 17 examples where B is the larger atom, and 6 where it is the smaller atom. In the case of the eutectic $Ag_{92}Te_8$, the Te is probably the larger atom, but the widely differing distances of approach in the crystal of Te make it impossible to estimate the size-factor.

The symbols are arranged so that the second element is the B element.

In all cases the size-factor is with reference to the A element.

two B atoms, but the pentagonal ring on either side can hold only one B atom if B-B closest neighbours are to be avoided. This permits a stacking sequence :



which accommodates 3B atoms in 12, or 25 atomic % of B, but the introduction of more B atoms must result in B-B closest neighbours. We can, thus, perhaps, understand a sudden increase in free energy in this region and it is perhaps significant that, of the 36 eutectic points which occur at 24, 25, or 26 atomic %, no fewer than 23 are systems where the electro-chemical factor is large, and this number would be increased if Ge and Sb

Table 2

Eutectic composition	Systems with B the larger atom, and size factor (%)	Systems with B the smaller atom, and size factor (%)
$A_{83}B_{17}$ Total number of eutectics 16	AgBa 51 AuNa 29 GaIn 33 BeCu 14 ZnU 13	AlCu -11 PrAu -21 FeC -39 LaMn -28 PbLi -11 MnAs -6 FeB -29 SbGe -16 KHg -54 MoSi -14 TiSn -3
$A_{82}B_{18}$ Total number of eutectics 15	CuAl 12 NiW 10 HgCs 75	FeP -15 MgAg -10 BaPb -20 CuAs -1 ThNb -21 PbSb -17 CeNi -31 NbSi -18 MgHg -7 VS -21 ZrSb -9 UV -10
$A_{81}B_{19}$ Total number of eutectics 16	CdNa 25 CuSb 14 MgPb 10 SiCe 55 NiSn 13	TlAs -26 BiAu -7 NiB ~-28 CaSn -29 UCr -17 MgGa -24 NiP -12 WC -44 SbMn -8 ThV -27 PdP -21

For the $A_{83}B_{17}$, $A_{82}B_{18}$ and $A_{81}B_{19}$ eutectics there are 34 examples where B is the smaller atom, and 13 examples where B is the larger atom.

The symbols are arranged so that the second element is the B element.

In all cases the size-factor is with reference to the A element.

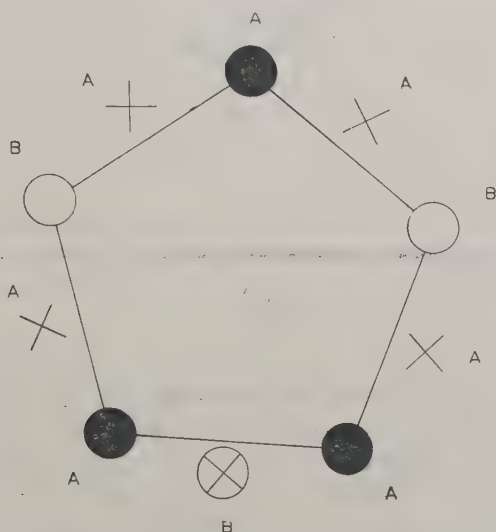
were regarded as electronegative in the systems CoGe, GeMn, GeFe, and CoSb. In this way, we can perhaps understand the peak at approximately 25 atomic % in the eutectic distribution curve.

The above discussion is admittedly speculative and incomplete. It is included to suggest a way in which the position of the peaks on the eutectic distribution curve may be interpreted on the assumption that they are due to the existence of bends on the G/C curves. The discussion has deliberately been confined to the icosahedral units and pentagonal chains because these avoid the introduction of nuclei for crystallization.

§ 10. TYPES OF LIQUID IMMISCIBILITY

As pointed out above (p. 389) the existence of a sharp valley in the $\Delta G/C$ curve leads to the formation of liquid immiscibility, unless solid phases intervene.

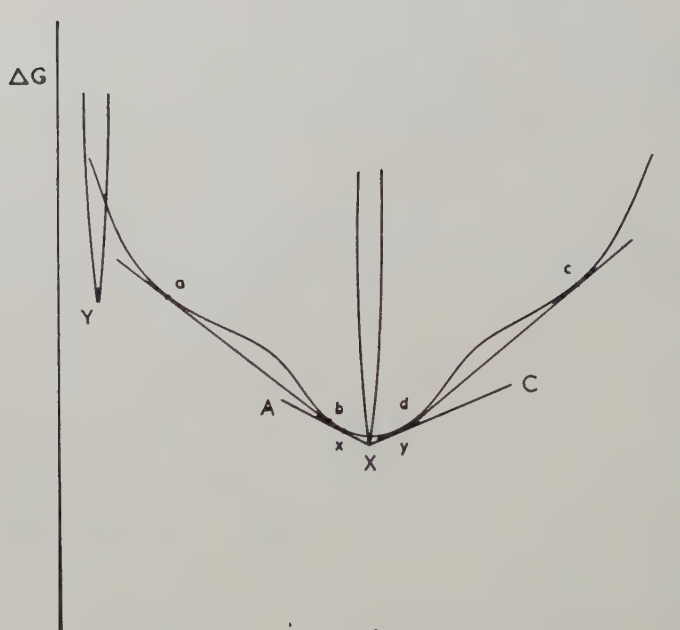
Fig. 13



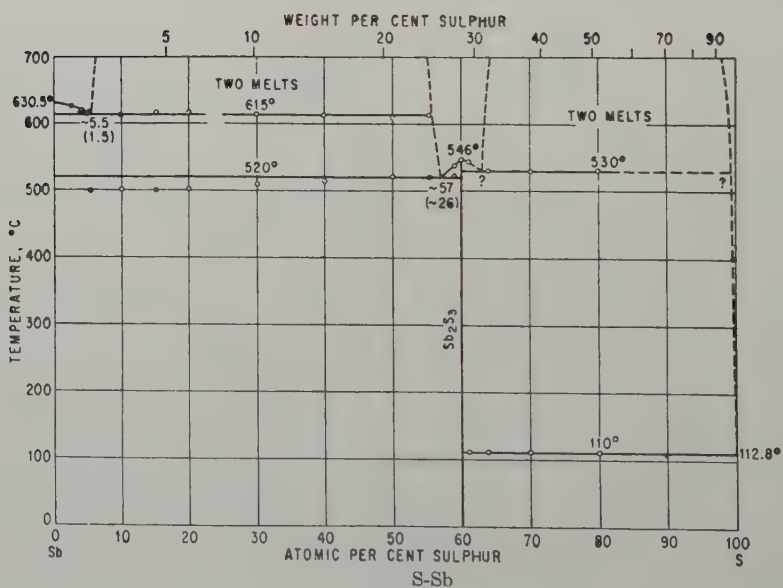
● A atoms, and ○ B atoms in one pentagonal layer. × A atoms in adjacent layer. ⊗ B atom in adjacent pentagonal layer.

We may consider first the case of fig. 14(a) where convenient atomic packing gives a marked trough in the $\Delta G/C$ curve for the liquid, and where a solid phase X exists whose composition is the same as that of the minimum in the curve for the liquid. In this case decreasing temperature will eventually produce a condition in which the ΔG curve for the solid falls slightly below the minimum as shown in fig. 14(a). At this temperature, alloys with compositions between X and y will consist of (Solid X + Liquid y) whilst those between y and d will consist of a single liquid phase, and those between d and c will consist of two liquid phases. A similar condition of affairs will exist on the opposite side of X , where two liquid phases will exist between a and b , a single liquid phase between b and x , whilst between x and X the alloys will consist of (Liquid x + Solid X).

Fig. 14



(a)



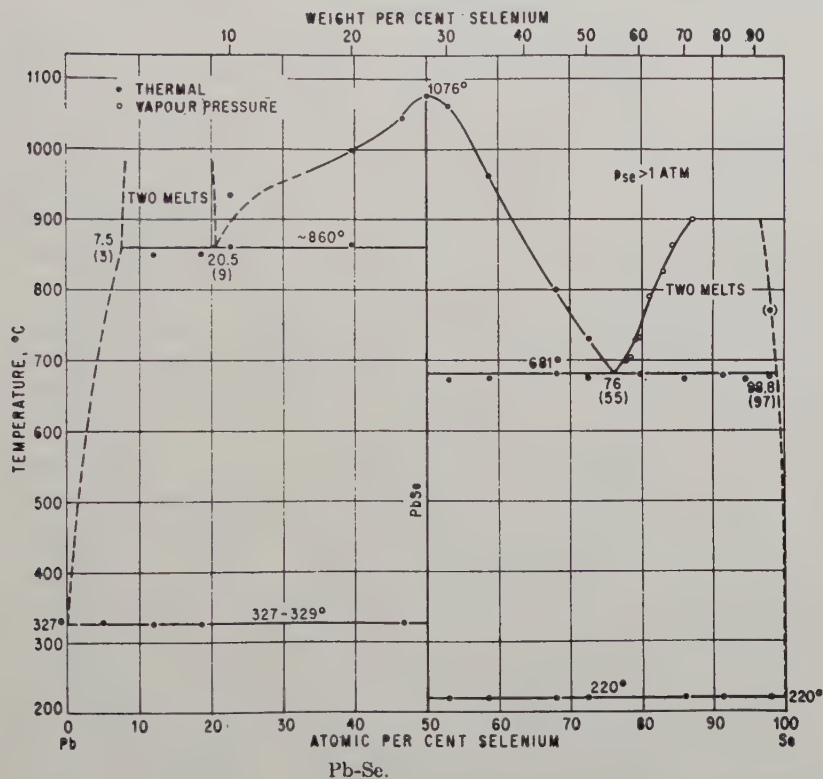
(b)

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Alternatively, if the ΔG curve for a solid phase Y lies slightly below ab , the region of liquid immiscibility will be replaced by a ($Y + \text{Liquid}$) field, and on lowering the temperature there will be a eutectic of ($Y + X + \text{Liquid}$). If on raising the temperature, the ΔG curve for Y rises above ab , the phenomenon of liquid immiscibility will appear.

These characteristics are shown most strikingly by some alloys of S, Se and Te. Figure 14(b) shows the system S-Sb which clearly resembles the case discussed above. In this case X in fig. 14(a) is the compound

Fig. 15



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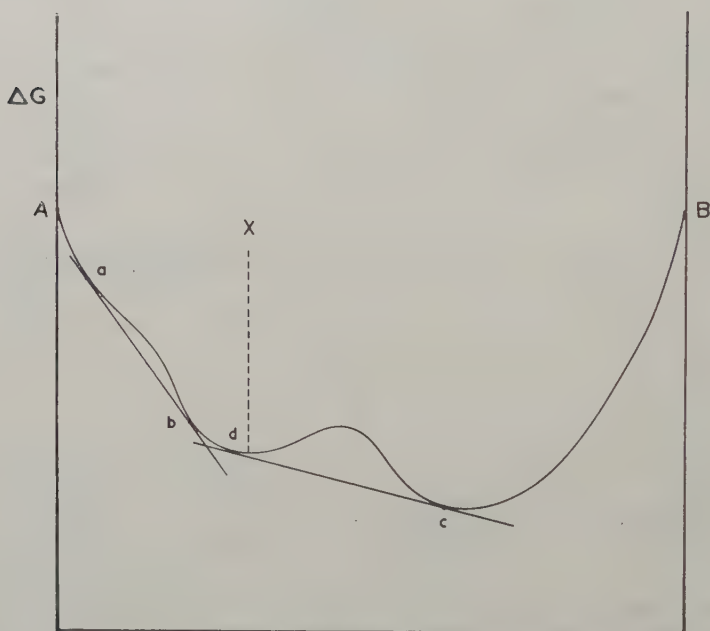
Sb_2S_3 in fig. 14(b), and Y is pure Sb. 520°C is the temperature of the ($X + Y + \text{Liq}$) eutectic of fig. 14(a), and 615°C is the temperature at which Y in fig. 14(a) lies on the projection of the straight line ba . The system AgSe is another example of this kind of diagram.

If the present interpretation is correct, the formation of immiscible liquids in this kind of system is not due to a reluctance of the two kinds of atom to pack together to form a liquid. On the contrary, they form a liquid of great stability (i.e. low ΔG in fig. 14(a)), and the liquid immiscibility results from the consequent inflection in the ΔG curve. In some

of these cases it is possible that there are definite compound molecules in the liquid, or definite ratios of oppositely charged ions. This may be the reason why the depression of the liquidus in Ag-rich AgSe alloys is not that given by van't Hoff's equation. It seems, however, quite possible that purely geometrical packing factors may lead to a sharp valley in the ΔG curve, with the resulting formation of immiscible liquids.

If in fig. 14(a) the compound X becomes increasingly stable, and the trough in the liquid curve is broader, the regions of liquid immiscibility will be displaced outwards from X . The system PbSe shown in fig. 15 appears to be an example of this kind.

Fig. 16



The above argument depends on the assumption that in fig. 14(a) the trough in the curve is such that a and c lie above b and d respectively. There is also the possibility of a curve such as that of fig. 16 where, on drawing the tangents, a is above b , but c is below d . In this case, if the compound X has the same composition as the minimum in the curve, the point d will lie to the left of X . On lowering the temperature the ΔG point for X will eventually meet the line dc , and the equilibrium diagram will be of the form of fig. 17, in which the compound X lies under and near to the edge of one of the regions of liquid immiscibility. There appears to be no simple example of this, but in the system PSn, the general effect is found with the complication of an additional compound in the region between the two fields of liquid immiscibility (see fig. 18).

Fig. 17

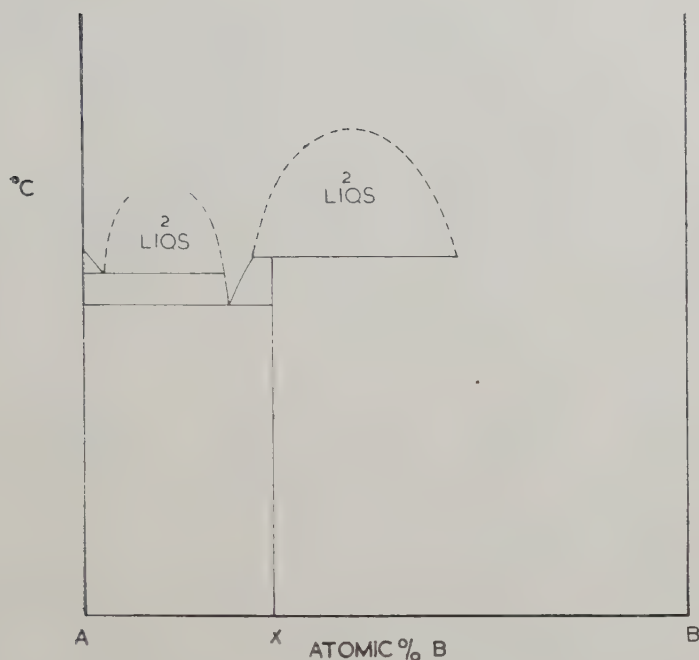
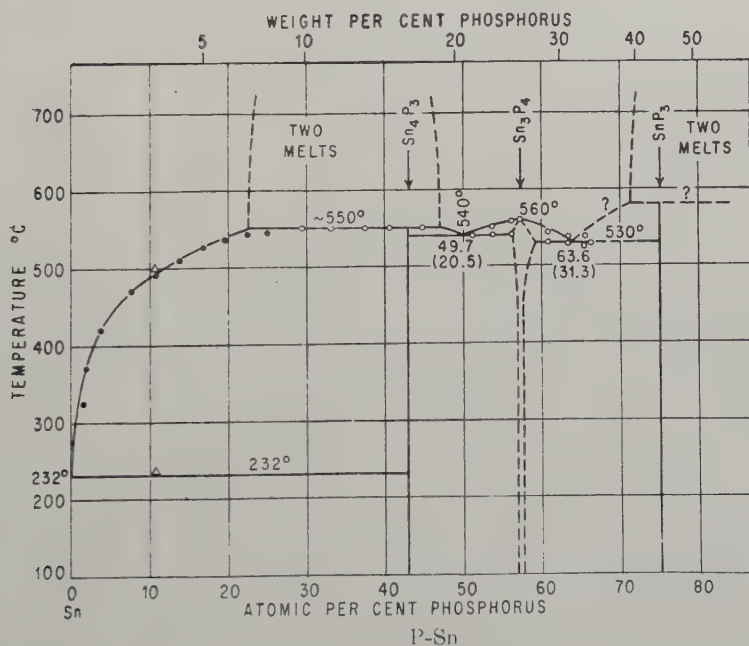


Fig. 18

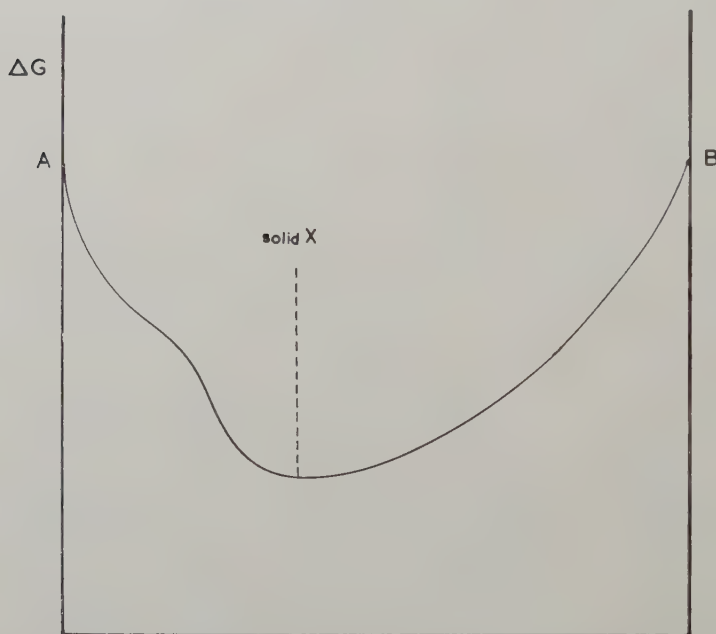


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It is clear that, if our interpretation is correct, the formation of two separate fields of liquid immiscibility requires inflections on both sides of the minimum in the curve of fig. 14 (a). If the inflection occurred on one side only as in fig. 19, the above argument would lead to the existence of a region of liquid immiscibility on only one side of the compound. This is a characteristic of systems such as CuSe (see fig. 20).

If our interpretation is correct, liquid immiscibility of the above types is to be distinguished from the more ordinary type for which the $\Delta G/C$ curves are of the form of fig. 21. Here, at each side of the diagram, the free energy first falls and then rises, which is an expression of the fact

Fig. 19

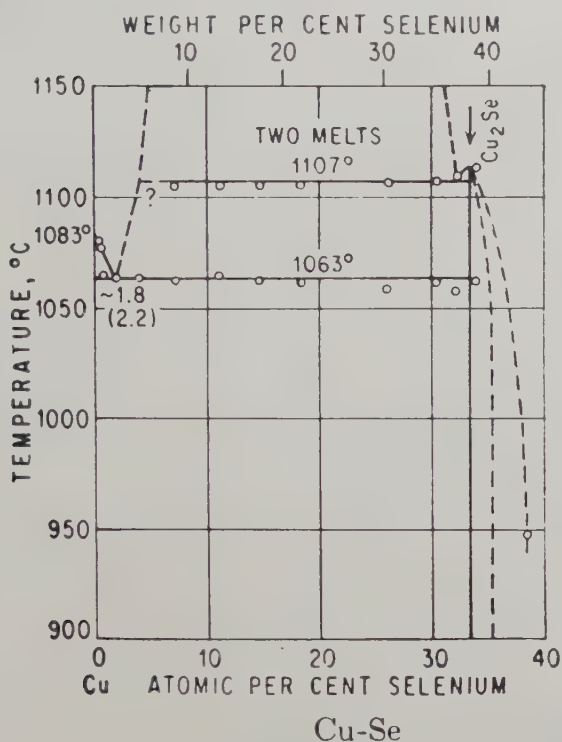


that the two kinds of atom 'do not like to mix'. In contrast to this, the liquid immiscibility referred to above results from the two kinds of atom having such a strong tendency to mix at a particular composition, that the free energy falls, and produces an inflection in the $\Delta G/C$ curve.

§ 11. OTHER EVIDENCE FOR ORDERED STRUCTURES IN LIQUID ALLOYS

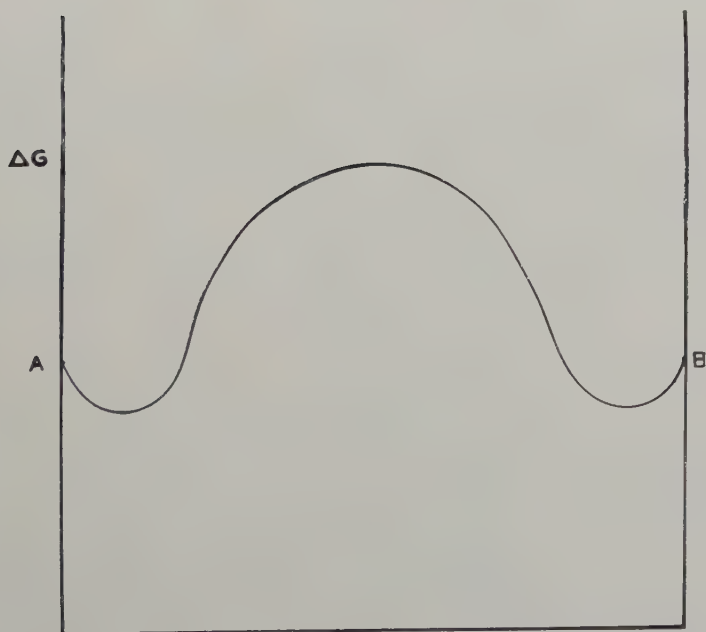
If the $\Delta G/C$ curves for liquid alloys contain inflections of the types discussed above, these should be revealed by irregularities in the curves connecting various physical properties with the composition. In connection with the electrical resistivity of the liquid alloy, two effects may be expected. On the one hand, the development of ordered structures at particular compositions should lead to minima at the compositions concerned. On the other hand maxima in the resistivity/composition curves

Fig. 20



Cu-Se
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Fig. 21



may be expected at compositions at which definite molecules or polar structures are formed with the conduction electrons bound into stable groups.

In a recent paper, Roll and Motz (1957) have examined the electrical resistivity of a number of alloy systems in the liquid state, and many of the isothermal curves show a maximum or minimum resistance at 25 or 32 atomic % of solute. These are two of the compositions corresponding to maxima on the eutectic distribution curve. Similar effects are shown in corresponding curves by other authors, and it is hoped to discuss these later.

The liquidus curves for the freezing of solid solutions should also show inflections if ordered structures exist in either the solid or the liquid solutions. If a system is chosen in which the solid solution is of negligible extent, any inflections in the liquidus curve may reasonably be taken to suggest ordered structures in the liquid. Examination of the very careful curves of Heycock and Neville (1897 a, b) suggests that some of these may be built up of segments with relatively sharp changes of direction. The conclusive establishment of this is a matter of difficulty, because highly accurate experimental data are required, and there is a natural tendency for authors to draw smooth curves through their experimental points. It is hoped to examine this question in detail later.

APPENDIX

The data from Hansen's text-book have been accepted with very few exceptions, and the following points may be noted:

(1) For alloys of Pu, several diagrams are reproduced on which eutectic compositions are indicated. These are described as being based on specimens weighing a few hundred milligrams, and we understand that further work is required before they are significant.

(2) The following eutectics (in atomic %) are not numbered in Hansen's book, but appear to be well established:

AuSn (6 Au)
 BiTl (7 Bi)
 CuSi (20 and 30 Si)
 MgZn (30 Zn)
 AuCd (30 Au)
 GeNi (28 Ge)
 CuIn (26 In)
 AlNi (24 Al)
 AuZn (34 Zn, and 37 Au)
 MnPd (27 Pd, and 32 Mn)
 AlMg (42 Mg)

(3) The following eutectics are included as the result of recent work in the authors' laboratory:

MnTi (10 Ti)
 FeTi (16 Ti)
 CuGe (22 Ge, and 37 Ge)
 AlFe (32 Fe, and 26 Fe)

(4) The following eutectics have been omitted either because of inconsistent results of different investigators, or because of uncertain evidence:

SiU (47 Si). The eutectics at 9 Si and 14 U have been accepted in the total number
 KSe equiatomic C.M.P. eutectic
 LaMg equiatomic C.M.P. eutectic
 AsSn (45 As)
 MnPt (40 Mn)
 CuTi (34 Ti). The eutectic at 43 Cu is accepted as well established
 AuBe (20 Be)
 AlLa (La-rich eutectic)
 LiNa (4 Li)
 AlU (6 Al)

(5) In the system AsTe the 25 As eutectic has been included because the original text suggests that the composition was established at least approximately, although figures were not given.

(6) The following equilibrium diagrams have been ignored:

BZr
 BeZr
 SiV
 SiW

(7) It may be pointed out that the present paper refers to eutectic points only; monotectic points have not been included.

ACKNOWLEDGMENTS

The authors must acknowledge the benefit received from discussions with Professor J. D. Bernal, F.R.S., and from Dr. J. W. Christian.

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CORRESPONDENCE

An Observation of Crack Formation in MgO

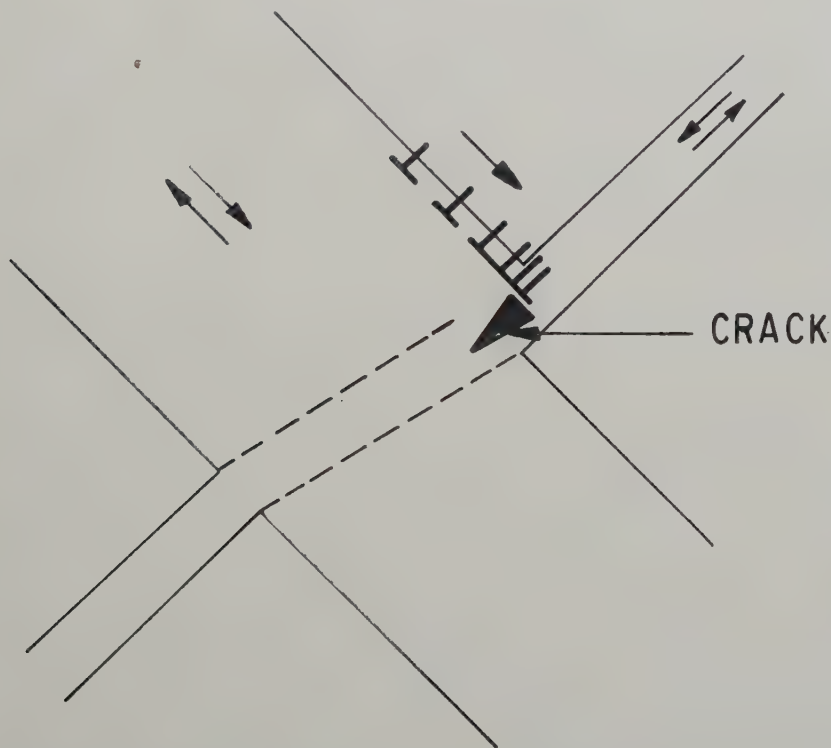
By W. G. JOHNSTON

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[Received March 7, 1960]

STOKES *et al.* (1959) have recently described the formation of cracks at the intersection of glide bands in MgO single crystals. Those authors proposed that under certain circumstances, edge dislocations moving on a (110) plane pile up at an intersecting glide band, and coalesce to form a Stroh-crack (Stroh 1955). It is the purpose of this note to present an observation of crack formation in MgO that supports in quite some detail the proposal of Stokes *et al.*

Fig. 2



Schematic drawing of the glide band intersection of fig. 1, showing the type of dislocation that is piled up.

In fig. 1 (Pl. 42) is shown a slit-type crack such as described by Stokes *et al.* The crack formed along the intersection of two glide bands in an MgO crystal that was deformed in $2\frac{1}{2}\%$ in compression, and it extended all the way through the $\frac{1}{8}$ in. square crystal. The crystal was compressed at a strain rate of 10^{-4} sec $^{-1}$, and the compression axis was parallel to the $\langle 100 \rangle$ crystal edge that appears in fig. 1. The crystal was then etched for 30 sec in sulphuric acid at 55°C. The dislocations in the intersecting glide bands, were predominantly edge dislocations, their Burgers vectors being parallel to the arrows alongside the bands.

The wide glide band intersects several lighter glide bands, and it is deduced from the offset of those light bands perpendicular to the wide band that they were present before the wide band formed. The light bands were possible obstacles for the wide band, and it is in fact seen that part of the wide band has been blocked by a light band, and that a crack has formed at the blocking point. The type of edge dislocation that would pile up at such a blocking point is depicted in fig. 2. That type of dislocation would lead to the formation of a Stroh crack that would spread into the wide band, as this crack appears to do.

The observation presented here supports the proposal of Stokes *et al.* for crack formation in MgO. However, it is not clear that conclusive proof for the operation of Stroh's mechanism for crack formation can be obtained from observation of dislocation distributions in a cracked crystal. It would seem that the only conclusive proof would be an observation of the actual coalescence of dislocations, such that as the dislocations disappeared, a crack would appear. Although such an observation may eventually be made by electron microscopic observation of a thin crystal, it does not seem possible by etch pit methods.

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Upper Limit to Anisotropy of Inertial Mass from Nuclear Resonance

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[Received April 14, 1960]

It has been pointed out by Bondi (1952) and Cocconi and Salpeter (1958) that if inertial mass is taken to arise from gravitational interaction with distant matter one would expect the concentration of matter near the centre of our own Galaxy to cause some anisotropy of inertia at the earth. This anisotropy might be as large as one part in 10^7 ; and Cocconi and Salpeter suggested that it could be detected from the shifts in atomic energy levels which might result. In a single-electron atom in a magnetic field parallel to the direction of the centre of the Galaxy they find that the energy of a $p_{3/2}$ state with magnetic quantum number $m_j = \pm 1/2$ would be altered by an amount $T \cdot \Delta M/5M$, where T is the mean kinetic energy of the electron and $\Delta M/M$ is the fractional difference between the inertial masses of a body (the electron) for accelerations parallel to the direction of the centre of the Galaxy, and perpendicular to it. A $p_{3/2}$ state for which $m_j = \pm 3/2$ would show an energy shift of equal magnitude in the opposite direction. If the magnetic field is perpendicular to the direction of the centre of the Galaxy then both these energy shifts would be reversed.

The high energy resolution obtained in studies of recoil-less resonance scattering of gamma rays suggests that this technique might provide a more sensitive method of searching for anisotropy of inertia, and in fact this idea has already been put forward by Cocconi and Salpeter (1960). In such an experiment one would look for changes in nuclear energy levels, and as the kinetic energy of the nucleon involved (in a shell-model picture) is of the order of 10 mev the effects would be expected to be larger than in the atomic case. If it is assumed that the same calculation of energy shifts applies directly both to the atom and the nucleus, it is already possible to put a tentative upper limit to the magnitude of $\Delta M/M$ for a nucleon of about 10^{-14} from the sharpness of the lines observed in ^{57}Fe , as Cocconi and Salpeter point out. We would like to suggest here that even more sensitive checks on anisotropy of inertia can be made by nuclear magnetic resonance and nuclear quadrupole resonance techniques.

In a pure magnetic resonance experiment on a nucleus with total angular momentum quantum number $I=3/2$, for example, the three magnetic dipole transitions between the magnetic sub-levels are normally taken to have the same resonance frequency. Anisotropy of inertia would

be expected to shift the levels having magnetic quantum numbers $m_I = \pm 3/2$ in one direction, and those for which $m_I = \pm 1/2$ in the opposite direction, turning the line into a triplet. With the direction of the magnetic field fixed relative to the earth, the spacing of the outer components of the triplet would vary with time as the angle between the magnetic field and the direction of the centre of the Galaxy changes. In practice one might either work with a liquid specimen and look for small diurnal changes in the breadth of the composite resonance line, or use a single crystal in which the line is already split by a weak quadrupole interaction and look for changes in the splitting. One could hope to detect easily changes of the order of 100 cycles/sec, corresponding to values of $\Delta M/M$ of about 10^{-19} . Even from the consistency of the original results of Pound (1950) on quadrupole interactions in magnetic resonance one can probably set an upper limit to the magnitude of $\Delta M/M$ of the order of 10^{-17} .

Similar experiments can be made using pure quadrupole resonance. With a nucleus having $I = 3/2$ a single resonance corresponding to transitions between the states with $m_I = \pm 3/2$ and $m_I = \pm 1/2$ is normally expected. Anisotropy of inertia would shift the upper and lower states in opposite directions, altering the resonance frequency by an amount depending on the angle between the axis of electrical symmetry and the direction of the centre of the Galaxy. Small shifts of this kind might be detected using a single crystal of a material in which the nucleus being studied may be situated at several chemically equivalent sites in the unit cell, the axes of electrical symmetry at these sites being equally inclined to a fixed direction in the crystal. Such a crystal can be oriented so that at a certain time of day all the axes make equal angles with the direction of the centre of the Galaxy (and possibly also with the plane of the Galaxy), when the resonance frequencies at all the sites would coincide; while a few hours later the angles made by the axes with this direction might vary over a wide range, at which time one would expect separation of the resonance frequencies to broaden the composite line observed. An experiment of this kind might be almost as sensitive as one using magnetic resonance; and again one can already set an upper limit to anisotropy of inertia from present data. In this case experiments with polycrystalline specimens are the most definite, for in these anisotropy of inertia should lead to broadening of the resonance for any orientation of the apparatus. Measured line breadths (Krüger and Meyer-Berkhout 1952) of 10 kc/sec with ^{63}Cu and ^{65}Cu (each a nucleus with an unpaired $p_{3/2}$ proton) thus put an upper limit to the magnitude of $\Delta M/M$ of about 2×10^{-17} .

It might be remarked that as we have applied the calculation of Cocconi and Salpeter without considering details of nuclear structure the above limits to $\Delta M/M$ are not to be considered precise. Nevertheless it would appear that a very sensitive search for anisotropy of inertia can be made by nuclear resonance methods; and that even from data already

available one can put an upper limit to anisotropy of inertia of the order of a few parts in 10^{17} , a limit lower by a factor of about 10^{10} than the anisotropy which one might expect from the theories of inertia of Sciama (1953) and Kaempffer (1958) based on Mach's principle.

ACKNOWLEDGMENTS

The author would like to thank Drs. G. A. P. Wyllie, W. K. Burton, G. M. Lewis and K. M. Guggenheimer for valuable discussions.

Note.—Since this paper was written it has been heard that a nuclear magnetic resonance experiment like the one suggested here is being performed at Yale University. Results already obtained (Hughes *et al.* 1960) set an upper limit of 10^{-20} to the magnitude of $\Delta M/M$.

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The Embrittlement of Molybdenum by Neutron Irradiation

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[Received November 24, 1959]

IN a recent series of experiments on EN2 steel Hull and Mogford (1958) studied the effect of neutron irradiation on the parameters σ_i and k_y in the Petch relation

$$\sigma_y = \sigma_i + k_y d^{-1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

between yield stress, σ_y , and grain diameter, $2d$. They found that irradiation increased the lattice friction stress, σ_i , but that k_y , which is a measure of the stress required to free a dislocation from its impurity atmosphere, was unaltered. This simple phenomenological description of irradiation hardening in EN2 steel makes it possible to predict its brittle fracture properties after irradiation once the dependence of σ_i on integrated neutron flux has been measured. For example, at a given temperature brittle fracture occurs if

$$(\sigma_i d^{1/2} + k_y) k_y \geq \beta \mu \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where β is a constant which is nearly unity, μ the rigidity modulus, and γ the effective surface energy for fracture (Cottrell 1958). For the special case of σ_i varying and k_y constant this reduces to

$$\sigma_i d^{1/2} \geq a \text{ constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a result which was verified experimentally by Hull and Mogford.

To establish whether or not the same simple type of irradiation embrittlement occurs in other body-centred cubic metals the writer has applied the same method as that used by Hull and Mogford to molybdenum. Twenty molybdenum tensile specimens, each having a different grain size, were prepared from an arc-cast ingot. The method of preparation and the tensile properties of unirradiated specimens from the same ingot have been described in an earlier paper (Johnson 1959). The specimens were placed in a sealed argon filled aluminium canister and irradiated in BEPO for six months. The irradiation temperature was $40^\circ\text{--}50^\circ\text{C}$ and the integrated epithermal neutron flux about 2×10^{19} n.v.t. Probably about 1 epithermal neutron in 10 had an energy greater than 1 mev.

The irradiated specimens were tested in a modified Hounsfield tensometer at a strain rate of $0.88 \times 10^{-4} \text{ sec}^{-1}$. Nine were completely brittle and careful metallographic examination showed that they had failed by

transcrystalline cleavage. The dependence of brittle fracture stress, σ_f , on grain size is shown in fig. 1. The results do not seem to fit the relation

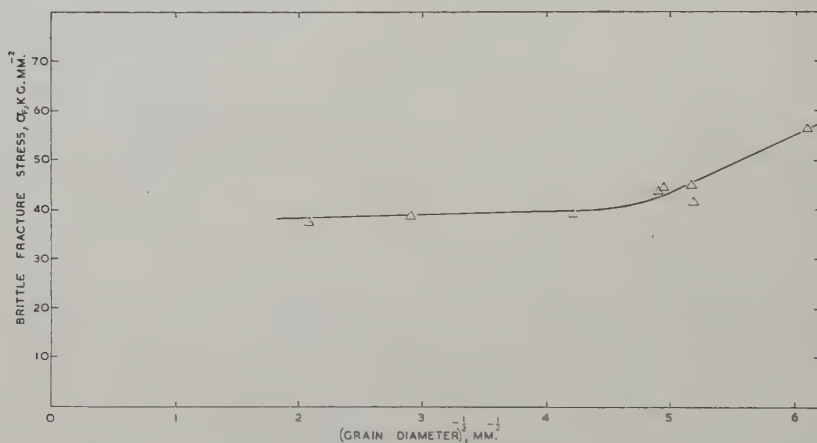
$$\sigma_f = \sigma_i + k_f d^{-1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which describes the behaviour of brittle unirradiated metals (e.g. Petch 1953). One result was rejected because the specimen fractured at a shoulder.

All of the remaining specimens showed pronounced yield points (fig. 2) and increased yield stresses. The changes in yield stress were greatest for large grain sizes (fig. 3) and hence cannot be due solely to a change in lattice friction stress. The strain to fracture and reduction in area at fracture were slightly decreased by irradiation for all grain sizes, but the fracture stresses were unchanged.

These results show clearly that the mechanism of irradiation embrittlement in molybdenum is more complex than that in EN2 steel.

Fig. 1

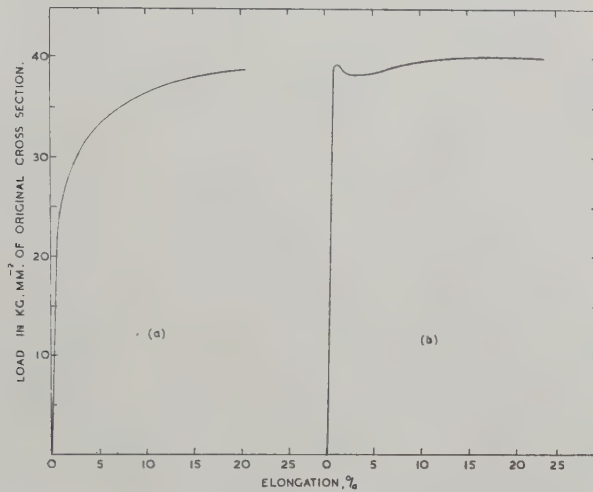


The effect of grain size on the brittle fracture stress of irradiated molybdenum.

Unfortunately, because the effects of irradiation cannot be described in terms of changes in σ_i and k_y , no straightforward interpretation of the results can be given. It seems likely that the effect of irradiation on the two materials is different because in molybdenum point defects created during irradiation can cause dislocation climb, whereas in EN2 steel climb is inhibited by a precipitate of cementite on the dislocations. If this were so all the edge dislocations in irradiated molybdenum would become jogged and the screws would tend to be wound up into spirals. This would have two effects on the mechanical properties. First, the presence of jogs on the dislocation lines in Frank-Read sources would make the sources more difficult to operate, and k_y would therefore increase. Secondly, if dislocation sub-boundaries were present they would become

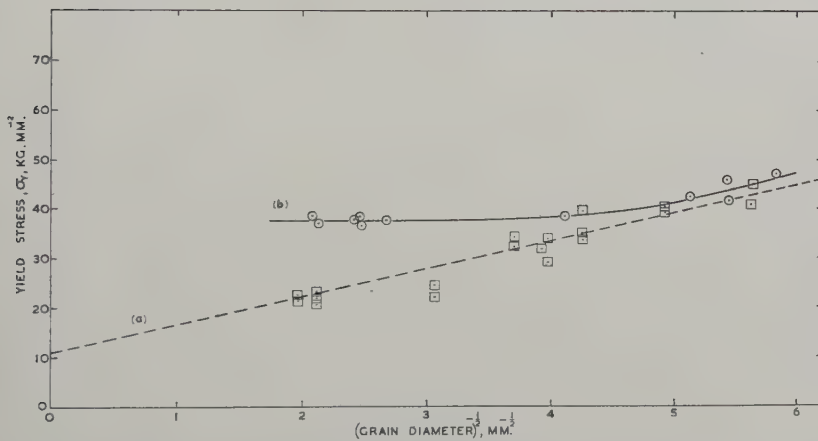
more opaque to slip dislocations and might then be expected to contribute to the mechanical properties in much the same way as grain boundaries.

Fig 2



Typical load-elongation curves for coarse grained molybdenum specimens, (a) before irradiation and, (b) after irradiation.

Fig. 3



The effect of grain size on the yield stress of molybdenum, (a) before irradiation, and, (b) after irradiation.

The specimens used in the investigation were examined for sub-structure by taking back-reflection x-ray photographs. Splitting of the spots showed that in coarse-grained specimens there were four or five sub-grains in a section through each grain and that the number of sub-grains per grain decreased with decreasing grain size. The yield stresses of the

irradiated specimens can therefore be explained semi-quantitatively by substituting estimated sub-grain diameters for grain diameters in eqn. (1). If this supposed strengthening of sub-boundaries were the only effect of irradiation the ductility of all the specimens would be increased whereas, in fact, some of all grain sizes become brittle. Because of the uncertainty in measuring the sub-grain diameters it is not possible to say from the results whether or not k_y has increased, but if we assume that it has, it helps us to understand the occurrence of brittle specimens because the brittle fracture criterion, eqn. (2), is very sensitive to changes in k_y . We are, however, left with the difficulty that no single value of k_y will satisfy eqn. (2) for all the sub-grain diameters simultaneously.

ACKNOWLEDGMENTS

This work was financed jointly by U.S. Navy Department, Contract No. N.62558(24)1177, and the Central Electricity Generating Board, and was carried out during the tenure of an I.C.I. Research Fellowship awarded by the University of London. The author is indebted to Professor J. G. Ball for his continued interest and encouragement, to Dr. H. M. Finniston and Mr. N. H. Hancock for the provision of irradiation facilities at A.E.R.E., Harwell, and to Mr. E. Bullen for taking the x-ray photographs.

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On Microcreep in Zinc Whiskers

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[Received April 6, 1960]

In a recent paper Cabrera and Price (1958) reported that microcreep was sometimes observed in zinc whiskers grown from the vapour when they were stressed in tension to elastic strains of the order of a few tenths of 1%, whereas large-scale plastic deformation did not occur until the elastic strain was raised to $\sim 1\%$. They concluded that whiskers in which creep occurred contained dislocations which were arranged so that they were difficult to move until the applied stress was fairly high. It was impossible to verify directly the existence of dislocations in these whiskers, because they were too small (1 to 7μ diameter) for etch-pit techniques (Coleman 1958) or x-ray transmission techniques (Webb 1958) to be applied and too thick to be examined by transmission electron microscope techniques (Hirsch *et al.* 1956).

In the present investigation of the mechanical properties of zinc whiskers and platelets, this difficulty was overcome by selecting only crystals which were thin enough to be examined by transmission electron microscopy, using a Siemens Elmiskop 1 operated at 100 kv and 10 to $40\mu\text{A}$ beam current. It was found that any dislocations which were present could be detected in crystals up to $\sim \frac{1}{2}\mu$ in thickness, provided the crystals were tilted with the stereo-control to produce maximum contrast. This paper describes those results of the investigation which pertain to microcreep.

Zinc whiskers and platelets of a wide range of sizes were grown from the vapour, in an atmosphere of argon, both by the technique of Coleman and Sears (1957) and by the technique of Price (1960). Those in the latter group were known to have grown at supersaturations in the range $\sigma = 0.5$ to 2, where $\sigma = (p - p_{\text{eq}})/p_{\text{eq}}$. Most of the crystals were cooled slowly from about 400°C to room temperature after growth, but one group was grown in a silica tube, then quenched in water at room temperature.

Sixty crystals, ranging in thickness from a few hundred angstroms to about one-half micron, were examined by transmission electron microscopy before being subjected to tensile tests. Their lengths varied from ~ 0.5 to 3 mm and their widths from 0.1μ to 2 mm. Each crystal was mounted with its largest faces perpendicular to the electron beam; electron diffraction patterns showed that these faces were always parallel to the basal plane. Of the sixty crystals studied, all but a very few were found

† National Science Foundation Post-doctoral Fellow, 1959–60.

to contain no dislocations. Examples of dislocation-free crystals are shown in figs. 1 and 2†. In no case was an axial screw dislocation ever observed. This does not, of course, eliminate the possibility that dislocations were present during growth but were removed from the crystals by climb during the cooling-down period. The only structural details which could be seen were growth steps. Occasionally surface corrosion pits developed on crystals which had been exposed to air for a long time (fig. 1).

In some crystals, however, dislocations were observed. Figure 3 shows a network of dislocations, lying predominantly on basal planes, which are believed to have been produced as a result of high stresses set up near the end of a large platelet where it was glued to the specimen holder. Most of these dislocations originate at the line of contact with the specimen holder and extend for a considerable distance into the platelet before finally emerging on a surface. This observation makes it clear that one must be extremely careful in handling and mounting these crystals.

After the dislocation arrangements in the crystals were determined, they were deformed in tension, either inside the electron microscope or in a high-sensitivity microtensile testing machine, capable of measuring extensions of less than $100\text{\AA}$ reproducibly (Marsh 1959). The results of tensile experiments carried out inside the electron microscope will be reported in another paper. The results of tests performed in the microtensile machine were as follows:

(1) Whiskers and platelets could be extended to high elastic strains, $\sim 2 \times 10^{-3}$ to 2×10^{-2} , before yield occurred, whether they contained dislocations or not, provided the strain rate was reasonably high ($\geq 10^{-5} \text{ sec}^{-1}$).

(2) Dislocation-free crystals showed no detectable plastic behaviour below the yield point when left for several hours at high elastic strains.

(3) Microcreep was always observed below the yield point in crystals containing dislocations. The creep strain usually reached a maximum value of 10^{-4} to 10^{-3} after about one hour at a constant elastic strain of 10^{-4} to 10^{-3} . This is in order of magnitude agreement with the observations of Cabrera and Price (1958) on crystals 1 to $7\text{ }\mu$ in thickness.

From these results it can be inferred that those whiskers tested by Cabrera and Price which showed microcreep also contained dislocations, which may have been grown in or introduced by stresses at the grips.

As fig. 3 shows, dislocations produced near the grips lie predominantly on basal planes, which are parallel to the axis of tension and therefore are not under a shear stress. Only those components which are on nonbasal planes will have a force exerted on them. It is suggested that, under a sufficiently high applied stress, these components will move, dragging the basal components with them and producing the observed microcreep. The creep stops when the dislocations have moved out of the crystal or have reached a more stable configuration. A higher stress is then required

† All figures are shown as plates.

to produce yield, either through the nucleation of a twin or through the production of new dislocations on nonbasal planes.

Studies of the processes of slip and deformation twinning in these crystals, using the transmission electron microscope technique, are in progress; the results will be reported later.

ACKNOWLEDGMENTS

I am indebted to Professor N. F. Mott, F.R.S., and Dr. F. P. Bowden, F.R.S., for their interest and encouragement and for making available the facilities of this laboratory. I am grateful to Dr. P. B. Hirsch for many useful discussions and for reviewing the manuscript. This work was carried out during the tenure of a post-doctoral fellowship awarded by the U.S. National Science Foundation.

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REVIEWS OF BOOKS

A Degree Physics, Part III, Optics. By C. J. SMITH. (London: Edward Arnold Ltd.) [Pp. 736.] Price £3 3s.

THIS book is a further volume in a series published under the title *A Degree Physics*, all by the same author. The first two volumes covered "General Properties of Matter", and "Electricity and Magnetism". The series is intended to cover rather more than is usually required by candidates taking physics at the B.Sc. General Degree level.

The book will undoubtedly be of great value to the class of students for whom it is intended. The style is readily understandable, and the diagrams are admirably clear. There is only one minor criticism which might be made; it is a pity that vector diagrams are not used more frequently in place of, or in addition to, a purely mathematical approach. The value of the vector diagram to the student is that it gives an immediate grasp of the problem, and shows clearly what happens when different quantities are varied. Examples of problems where vector diagrams might have been used with advantage occur on pages 47, 462, 469, 544, 570, 574 and 582. The usual phase amplitude diagram for circular division of a wavefront (page 569) is not given at all. The Cornu spiral, appropriate to strip division of a wavefront, is discussed, but it is first introduced as a plot of the Fresnel integrals and not as a phase amplitude diagram. This approach *via* the Fresnel integrals seems unnecessarily difficult at this fairly elementary level.

Quite a large part of the book is devoted to geometrical optics, including a detailed treatment of aberrations. Possibly the choice of subject matter was dictated by the requirements of a particular examination syllabus. If so, it seems a pity that so much geometrical optics should be demanded, for this subject, though technically important, seems to be of less educational value than physical optics. In physical optics, the student meets new methods and concepts which are of importance in many branches of physics, including modern physics. Geometrical optics, on the other hand, is a more or less self-contained subject and one, moreover, which any physicist should be able to learn quite easily if he should ever need to use it. With the constant expansion of knowledge examination syllabuses should be frequently revised, and something left out to make room for the new. Much of geometrical optics would seem to be overdue for omission.

The collections of examples at the end of each chapter form a valuable part of the book, and the answers to these are provided. B. H. B.

Physics of the Earth's Interior. By BENO GUTENBERG. (Academic Press.) [Pp. 226.] Price \$8.50.

THIS book is the first volume of the *International Geophysics Series*. It was published a few weeks before the lamented death of its author. For 50 years he has been not only one of the foremost workers in seismology, but also the author and editor of books bringing together and summarising our knowledge about the earth. The first of these was the enormous *Handbuch der Geophysik*. In this the wonder was that, even in Germany, so much could be written about a subject of which so little was known. The present book gives an admirable review of all that is now known about the inside of the earth in a mere 226 pages.

The subject is the interior of the earth; in keeping with this, topics connected with the crust of the earth, such as mountain building and isostasy are concentrated in one chapter near the start of the book. The main theme is the

deduction of the properties and state of the materials within the earth from the study of seismology, gravity and other physical observations at the surface. The detail with which the various topics are treated has been influenced by Gutenberg's own interests: the emphasis throughout is strongly on the physical side, chemical considerations and even the chemical nature of the materials concerned being barely mentioned.

The book should form a valuable introduction to the study of the earth's interior and a starting point from which the reader can appreciate the papers appearing in the journals.

E. C. B.

Les Traceurs Radioactifs en Métallurgie Physique. By C. LEYMONIE. (Dunod.) [Pp. 240.] Price 32 NF, about £2 6s.

THIS is an excellent little book dealing with the use of radioactive tracers in metallurgy and metal physics. About one-third of the book is devoted to the measurement of diffusion coefficients and many excellent tables of values are included and an adequate discussion given of the various values obtained. This will make it an excellent reference for the latest values up to about the end of 1958. Chapters are also devoted to the study of segregation in castings and in the solid state, to corrosion and oxidation of metals and to the study of the equilibrium between vapour and a condensed phase. Some new points are made in discussing the results of various workers and the author is to be congratulated on his familiarity with Russian work.

This book will appeal to the specialist and would be of use to anyone interested in applying tracer techniques. However, it is expensive for what it contains. The preparation is good but there are a number of misprints and it is annoying to find the name of one very eminent physicist continuously mis-spelt.

A. K.

Introduction to Mathematical Physics. By WILLIAM BAND. (Princeton, N.J.: Van Nostrand Co. Inc.) [Pp. 326.] Price £2 14s. 6d.

THIS book of about 325 pages surveys most of the main topics of mathematical physics. Starting from vector and tensor analysis, it works through the dynamics of continuous media to the kinetic theory of gases and classical electrodynamics. The last third of the book is concerned with the theory of relativity and wave mechanics.

No student would expect to learn so many subjects by reading so few pages. However, the book is clearly written, and it is certainly of value as a reference book or dictionary of mathematical physics in which the initiated can find concise discussion and useful formulae.

J. H.

Theory of Elasticity. By L. D. LANDAU and E. M. LIFSHITZ. Translated by J. B. SYKES and W. H. REID. (Pergamon Press, 1959.) [Pp. 134.] Price £2.

THIS impressive book is Volume VII of the splendid series of texts on Theoretical Physics by Landau and Lifshitz. It deals concisely with a restricted number of topics which have been selected primarily on account of their interest to physicists.

In Chapter I the authors derive the fundamental equations of infinitesimal elastic theory, under both isothermal and adiabatic conditions, and include a brief discussion of the elastic properties of crystals. Chapter II gives an account of the equilibrium of rods and plates, deriving the basic equations from first principles. Chapter III deals with elastic waves in isotropic and anisotropic media, surface waves, and the vibration of rods and plates. Chapter IV contains sections on thermal conduction and viscosity in solids, and on the absorption of sound.

Throughout the book the theory is illustrated by well-chosen problems (about 80 in all), in which the method of attack is sketched and the result quoted but left for the reader to derive. This method enables the authors to pack in an enormous amount of material of great interest.

The reader is assumed to be on familiar terms with vectors, tensors, potential theory, and thermodynamics. Unsuitable for a beginner, the book will be of great value, in its power and freshness, to readers already acquainted with the subject. The translation is excellent and the layout clear and pleasing.

E. R. L.

The Classical Theory of Fields. (Course of Theoretical Physics, Vol. 2.) By L. D. LANDAU and E. M. LIFSHITZ. Translated by Morton Hamermesh. (Addison-Wesley Publishing Co. Inc. and Pergamon Press.) [Pp. 354.] Price £3 10s.

THE second edition of the second volume of the authors' Course in Theoretical Physics was excellently translated in 1951, and is now re-issued in a binding uniform with the other volumes. In the first forty pages, the transformations and mechanical equations of special relativity are deduced from the principles of a finite invariant maximum signal velocity and of least action, while in the rest of the book, the electromagnetic and gravitational fields which carry the signals are discussed. The equations of motion of the fields and of particles in the fields are derived from the action principle and invariance considerations, and the Riemannian world geometry necessary for the gravitational case is explained very clearly. There are applications, or rather specializations, to static solutions, wave motion (including, in a chapter on optics, the geometrical limit and examples of diffraction) and radiation problems.

The treatment of the two fields in the same way is logical and illuminating, particularly since it is uncommon in text-books in this country. The book gives an impression of formality at a first reading, which is partly due to the nature of the subject and the deductive presentation; but in fact, the physically interesting applications are treated quite fully, being disguised by the label 'problems' and small print. This possibly reflects a different method of teaching in Russia. The volume's place in the Course as a whole will become clearer when the volume on macroscopic electrodynamics appears. At present one can say that it forms very valuable additional reading to a course on electromagnetic theory, and a first-rate introduction to the rather esoteric subject, as it is often considered, of general relativity.

D. J. C.

Recent Research in Molecular Beams. Edited by I. ESTERMANN. (New York: Academic Press.) First edition. [Pp. 190, 80 diagrams, 15 tables.] Price £2 12s.

THE molecular beam technique has progressed a long way since the basic principles were laid down by Otto Stern and his collaborators in Hamberg in the early 1920's, and most of the problems listed by Stern at that time as suitable for molecular beam investigation have now been solved with considerable success by techniques which can be traced back to roots planted during the early period. This volume contains a collection of ten papers, all of them written by research workers active in the fields concerned, dedicated to Otto Stern on the occasion of his 70th birthday as a public recognition of the way they have been stimulated by his personality and his work.

In the first paper I. Estermann reviews the early molecular beam work in Hamberg and traces the development of the technique in the 1930's. Recent research with radioactive atoms is reviewed in papers by W. Nierenberg and

V. Cohen, and various aspects of accurate atomic and nuclear resonance experiments are covered in three papers by V. Hughes, P. Kusch and N. Ramsey. Applications of the beam technique to chemistry are discussed by S. Datz and E. Taylor, scattering at solid surfaces is reviewed by F. C. Hurlbut and new work on the velocity distribution in atomic potassium beams is described by P. Marcus and J. McFree. The final paper is on a Stern-Gerlach experiment with polarised neutrons.

The treatment in most of the papers is by no means comprehensive but the book should be very useful to the beam specialists as an addition to N. Ramsey's text-book on the subject. The general reader will find the reviews an excellent source of recent data and an introduction to modern beam techniques.

K. F. S.

Introduction to Quantum Field Theory. By F. MANDL. (Interscience Publishers.) [Pp. 202.] Price £1 14s.

THE many textbooks now in existence dealing with quantum field theory are mainly addressed to the elementary particle physicist and develop the subject in considerable detail. Here is a book treating the basic ideas of second quantization, Feynman graphs, and renormalization theory, in as simple a manner as possible, accurately in terms of its level of sophistication, and with great clarity. It will serve as simple first reading for everyone and as a convenient account of field theory techniques for those to whom the subject is an occasional aid rather than a prime interest. This reviewer's only regret is that more attention has not been given to the qualitative ideas that underly the field theoretic formalism, and in particular to the nature of the vacuum. The backdrop of modern physics is not an empty void but a chaos of fluctuations and most of the characteristic field theory phenomena find their origin in this fact.

J. C. P.

Analysis of Deformation. Vol. IV. Waves and Vibrations. By K. H. SWAINGER. (London: Chapman & Hall, Ltd., 1959.) [Pp. xxvii + 370.] Price £3 15s.

DR. SWAINGER believes that classical theories of elasticity, plasticity and fluid flow are wrong at various points. This is the fourth volume of his attempt to correct them. Unfortunately he has cast his work into a form which might have been designed to give maximum difficulty to the reader. He invents his own notation for every quantity concerned (the summary of "Principal Notation" occupies six pages), uses dyadics, 'triadics' and 'quadadics' instead of Tensors, employs words with novel restricted meanings of his own, and writes in a contorted and obscure style.

The present volume deals with body and surface waves in isotropic fluids and elastic, visco-elastic or plastic solids. There is also a long chapter on geophysics, containing the author's theories of the constitution of the earth.

E. R. L.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

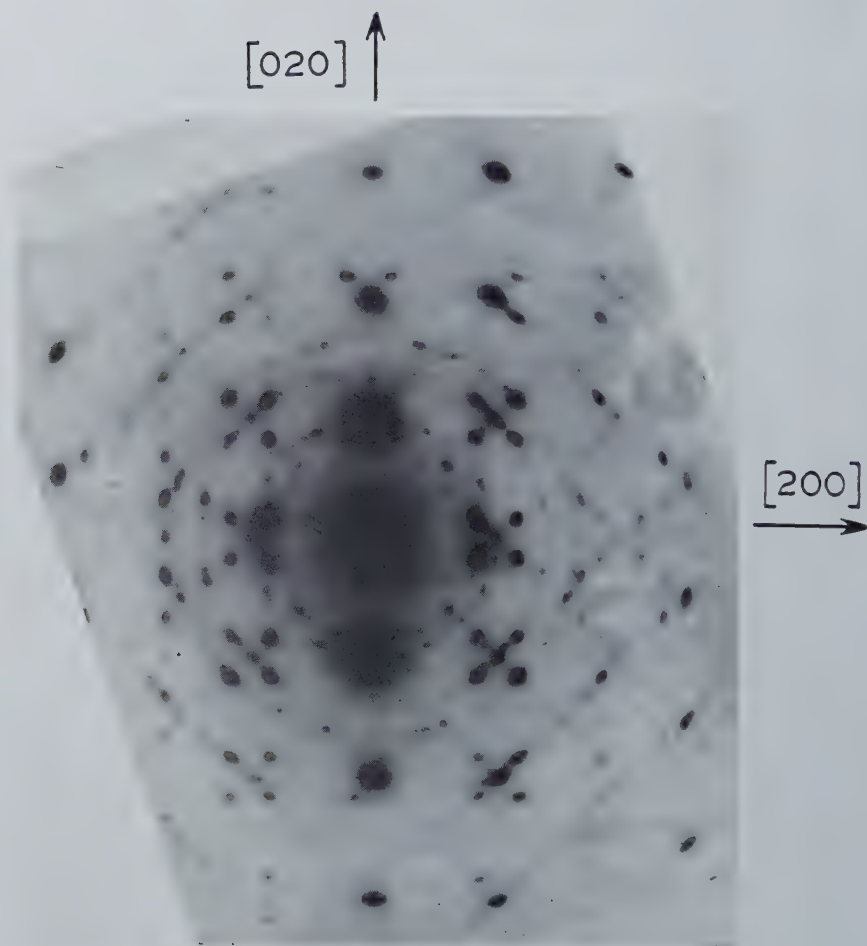
Fig. 1

$[220]\uparrow$



Electron micrograph of 'thick film' of 81%Ni-19%Fe. $\sim 600\text{ \AA}$ deposit on NaCl (100) at 320°C . Bright field illumination. Electronic magnification : $40\,000\times$.

Fig. 2



Selected area diffraction of 81%Ni-19%Fe film. About 7° inclination to $[001]$ zone axis. Many extra spots caused by twin lattices and double diffraction. Asymmetry of pattern caused by specimen deformation and 'effective aperture' of the electron microscope.

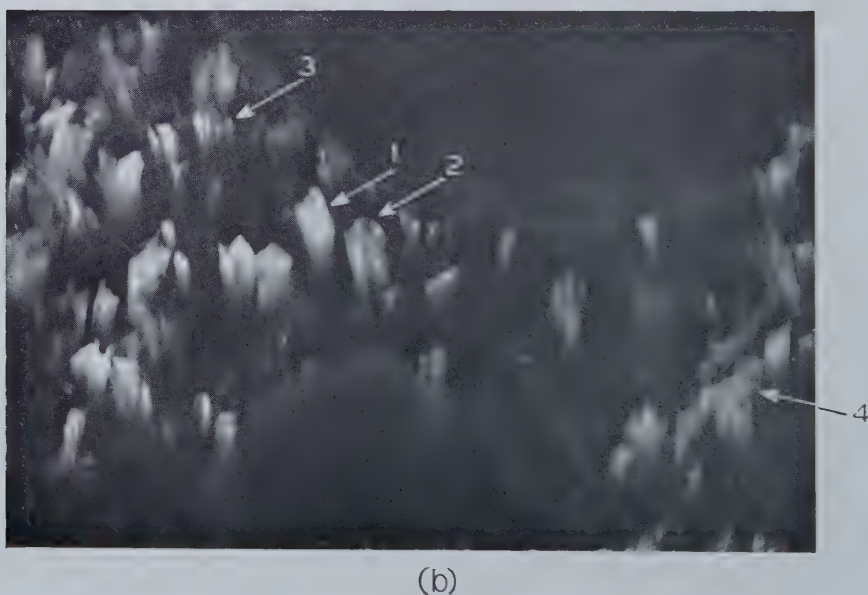
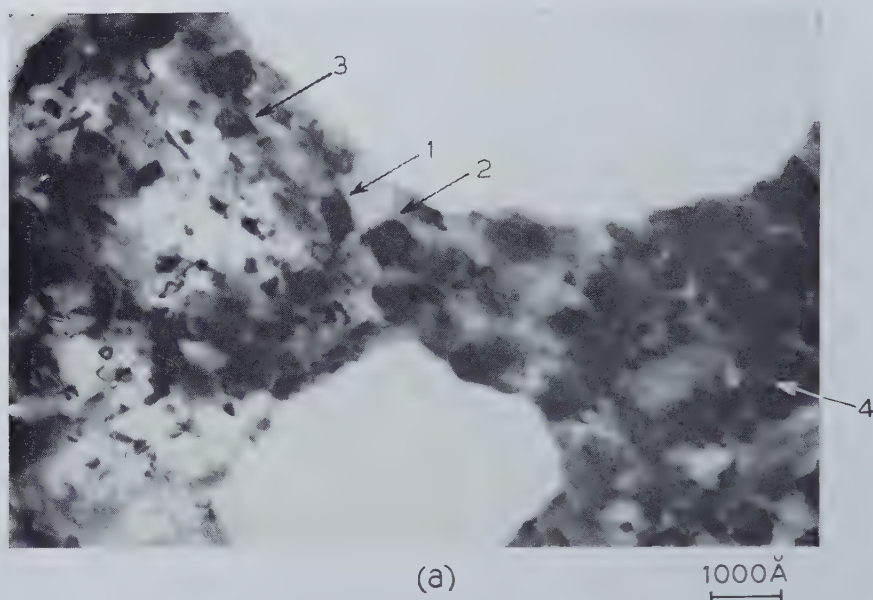
Fig. 8



1000 Å
└────────┘

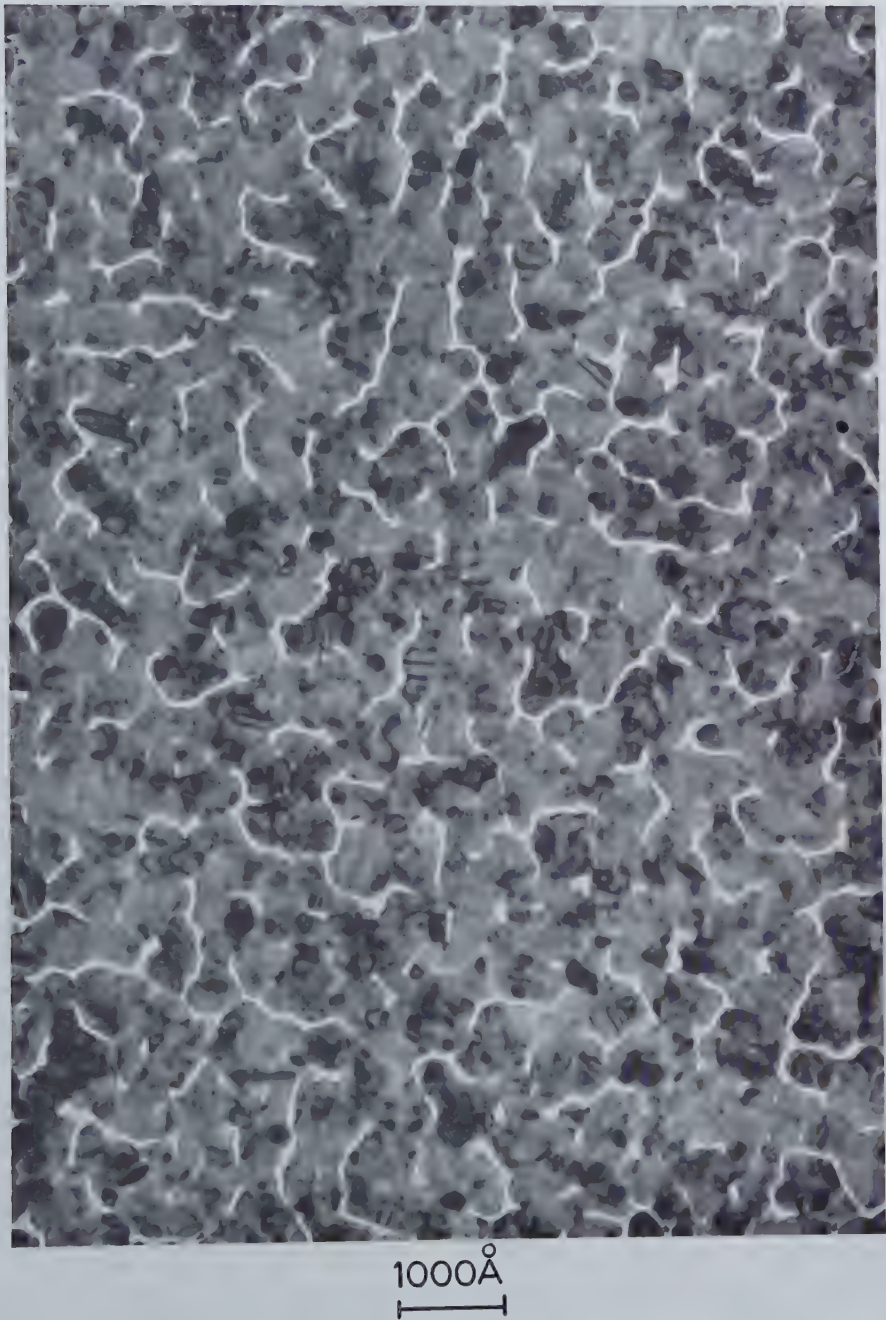
Electron micrograph of 'thick film' of 81%Ni-19%Fe. ~ 600 Å deposit on NaCl (100) at 320°C . Dark field illumination from both twin spots and double diffraction spots. Electronic magnification: $20\,000\times$.

Fig. 9



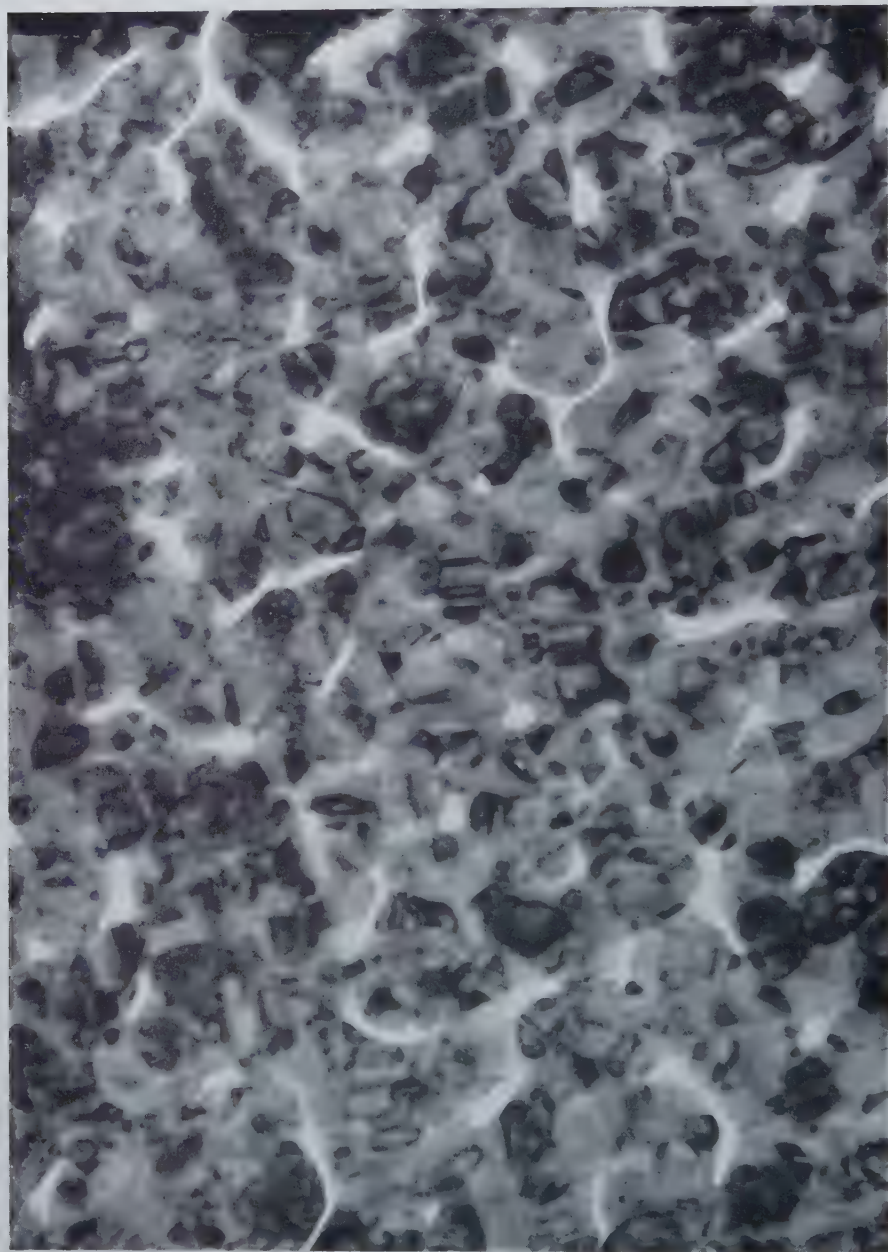
Electron micrographs of 'thick film' of 81%Ni-19%Fe after etching to 100–200 Å thickness. Electronic magnification: 20 000 $\times$. (a) Bright field illumination. (b) Dark field illumination from twin spots from two of the four twinned lattices. Several twinned regions indicated by numbered arrows.

Fig. 10



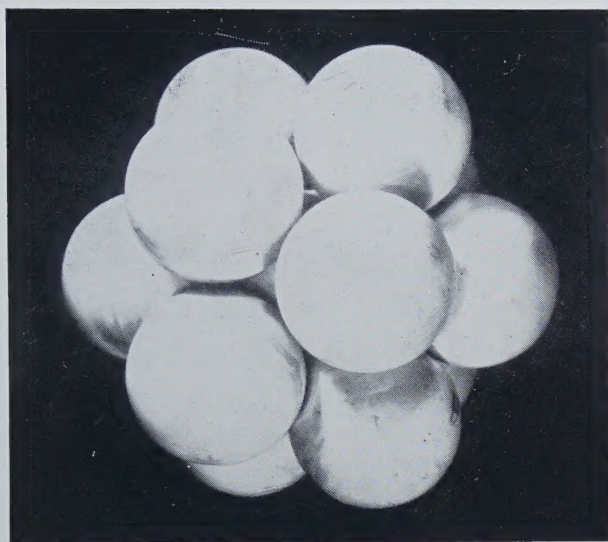
Electron micrograph of 'thin film' of 81%Ni-19%Fe. ~ 100 - 200 Å deposit on NaCl(100) at 320°C . Bright field illumination. Electronic magnification: $20\,000\times$. A crystallite made up of twin bands is located near the centre of the micrograph.

Fig. 11



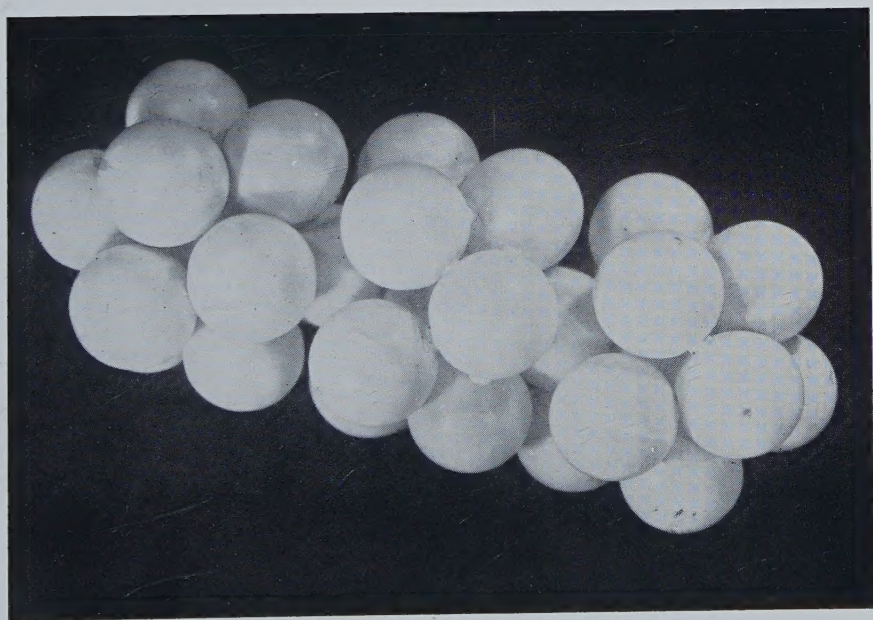
Electron micrograph of 'thin film' of 81%Ni-19%Fe. ~ 100 -200 Å deposit on NaCl (100) at 320 °C. Bright field illumination. Electronic magnification: 40 000 $\times$.

Fig. 11



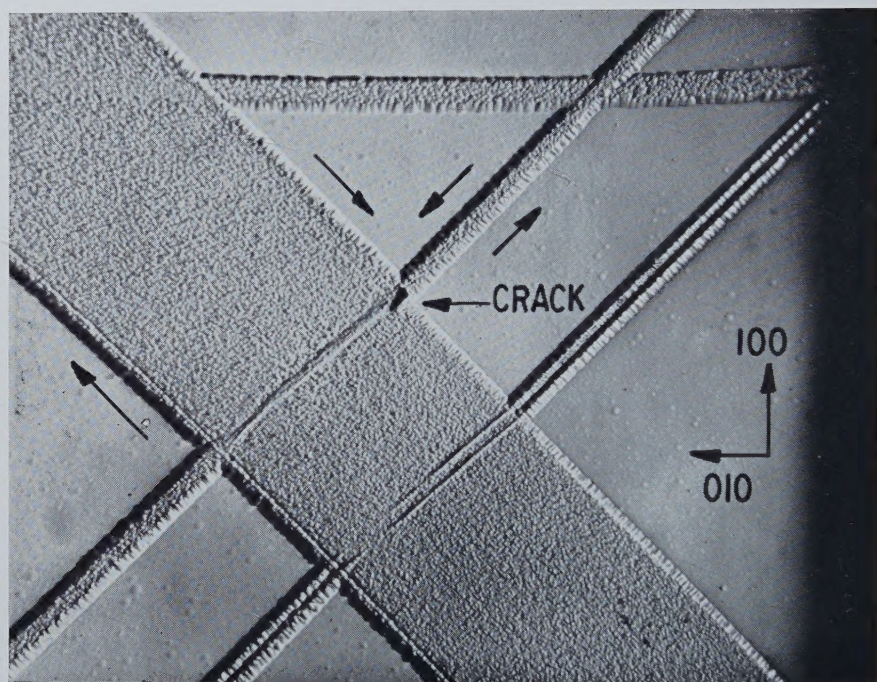
The Frank unit.

Fig. 12



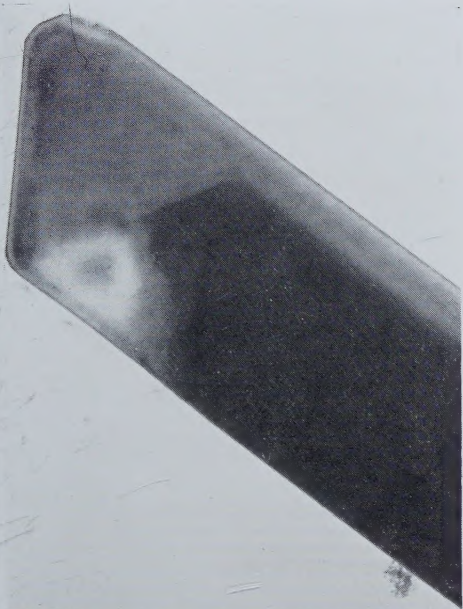
To illustrate the formation of pentagonal chains.

Fig. 1



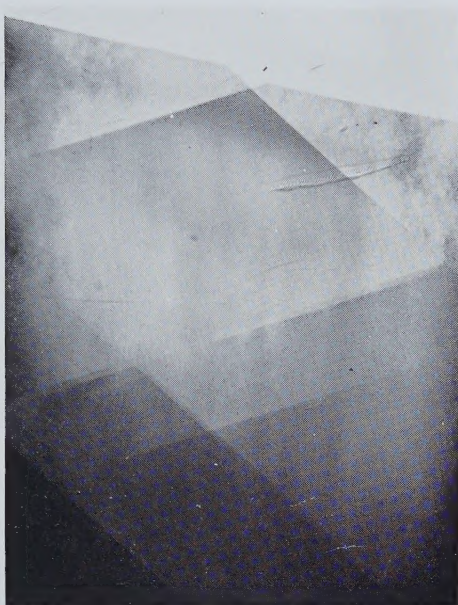
Crack at the intersection of glide bands in a MgO single crystal. The arrows alongside the bands indicate the shear within the bands. The crack has not been re-touched. Magnification: 500.

Fig. 1



0.5 μ

Fig. 2

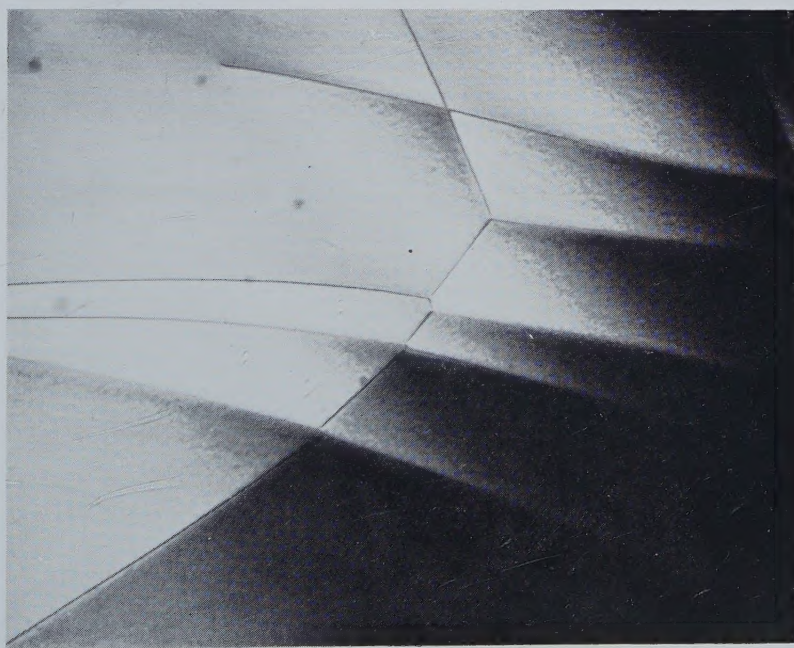


1 μ

Dislocation-free zinc whisker. The basal plane is parallel to the plane of the paper.

Dislocation-free zinc platelet. The growth steps are parallel to $\langle 11\bar{2}0 \rangle$ directions.

Fig. 3



1 μ

Dislocations, lying predominantly in basal planes, in a zinc platelet.

